

Synthesis and Magnetic Susceptibility of New Bimetallic, Tetranuclear and Octanuclear Complex Ions Containing Molybdenum(VI)/Tungsten(VI) and Chromium(III)/Rhodium(III). Crystal Structures of $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$, $\{[\text{MoO}_4\text{Rhcyclam}]_2\}(\text{ClO}_4)_2$ and $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$

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The synthesis, spectroscopic and magnetic properties of new types of bimetallic, tetranuclear and octanuclear complexes containing $\text{Mo}^{\text{VI}}/\text{W}^{\text{VI}}$ and $\text{Cr}^{\text{III}}/\text{Rh}^{\text{III}}$ are described. The crystal structures of $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$, $\{[\text{MoO}_4\text{Rhcyclam}]_2\}(\text{ClO}_4)_2$ and $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$, where cyclam = 1,4,8,11-tetraazacyclotetradecane have been determined from X-ray diffraction data.

$\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ crystallizes in the monoclinic space group $P2_1/n$ with two formula units in a cell of dimensions $a = 10.051(1)$, $b = 15.162(2)$, $c = 12.244(1)$ Å, $\beta = 104.001(8)^\circ$. The structure was refined to a final R -value of 0.064 for 2133 independent intensities. $\{[\text{MoO}_4\text{Rhcyclam}]_2\}(\text{ClO}_4)_2$, which is isomorphous with the chromium analogue and has cell dimensions $a = 9.858(2)$, $b = 15.269(2)$, $c = 12.373(2)$ Å, $\beta = 105.203(9)^\circ$, refined to a final R -value of 0.036 for 4070 independent intensities. The cations are centrosymmetric dimers with almost planar eight-membered $(\text{Mo}-\text{O}-\text{M}-\text{O})_2$ ($\text{M} = \text{Cr}$ or Rh) rings. Molybdenum is tetrahedrally coordinated to four oxygen atoms.

$\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ crystallizes in the orthorhombic space group $Pbcn$ with four formula units in a cell of dimensions $a = 19.572(2)$, $b = 24.347(4)$, $c = 16.601(2)$ Å and refined to a final R -value of 0.054 for 2454 independent intensities. The cation has two-fold symmetry and is built up about a distorted cube of tungsten and oxygen atoms. The cyclam ligands in all three complexes have a folded configuration in which alternate amine hydrogen atoms are on opposite sides of the macrocyclic ring.

The magnetic susceptibilities of the chromium complexes reveal that they are weakly antiferromagnetically coupled. For the bimetallic tetranuclear complexes the J -values are 0.78 and 2.08 cm^{-1} for the perchlorate salt and the iodide salt, respectively. For the octanuclear bimetallic tungsten complex J is 8.41 cm^{-1} .

In a recent publication¹ we reported the syntheses of novel types of octanuclear complexes, $\{[\text{Mo}/\text{WO}_4\text{Cr}/\text{Cobispictn}]_4\}(\text{ClO}_4)_4 \cdot n\text{H}_2\text{O}$, with $\text{Mo}^{\text{VI}}_4\text{O}_8^{8+}$ or $\text{W}^{\text{VI}}_4\text{O}_8^{8+}$ as central, cubanoid cores surrounded by four bridging entities of $[\text{O}_2\text{Crbispictn}]^-$ or $[\text{O}_2\text{Cobispictn}]^-$. The ligand bispictn on the trivalent metal was the tetradentate amine ligand N,N' -bis(2-pyridylmethyl)-1,3-pro-

panediamine. To find out if the synthetic method has general validity, we have replaced bispictn with 1,4,8,11-tetraazacyclotetradecane, cyclam, but have otherwise used the same procedure as before. In the case of tungsten, we got a similar octanuclear, bimetallic complex with a central cubanoid core, $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot n\text{H}_2\text{O}$. In the case of molybdenum we got a tetranuclear, bimetallic complex $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$, with two $\text{Mo}^{\text{VI}}\text{O}_4^{2-}$ groups as bridging

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entities between two chromium ions. A complex of similar structure was obtained when chromium was replaced by rhodium.

Experimental

Syntheses. Caution: Some of the described compounds are isolated as perchlorate salts and should be handled as potentially explosive compounds.

Starting materials. $(\text{NH}_4)_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$,² $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$,³ $2\text{HCl}[\text{Mo}_6\text{Cl}_8]\text{Cl}_4\cdot 8\text{H}_2\text{O}$,⁴ K_2WCl_6 ⁵ and *cis*-[RhcyclamCl₂]Cl⁶ were prepared according to methods described in the literature. The preparations of *cis*-[Crcyclam(OH)(H₂O)](ClO₄)₂ and *cis*-[Crcyclam(OH)(H₂O)]I₂·2H₂O have been published previously.⁷

cis-[Rhcyclam(H₂O)₂](CF₃SO₃)₃. Solid *cis*-[RhcyclamCl₂]Cl (1.06 g, 2.59 mmol) was treated with triflic acid (5 ml) at 110 °C for 4 h. At the same time a nitrogen flow was maintained to remove the hydrogen chloride vapour. Ether was then added to precipitate [Rhcyclam(CF₃SO₃)₂](CF₃SO₃). This crude product was washed with ether and suspended in water (75 ml). The suspension was heated nearly to boiling point, and the temperature was maintained for 10 min before the reaction mixture was left for 3 days at room temperature. By then it was filtered, and the solution was concentrated by evaporation. Ether was added again, and the new solid was filtered. Yield 1.91 g (94%). Anal. Calcd. for [Rh(C₁₀H₂₄N₄)(H₂O)₂](CF₃SO₃)₃: C 19.85, H 3.59, N 7.12. Found: C 19.92, H 3.49, N 7.29.

Bimetallic complexes

$\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**1**) *cis*-[Crcyclam(OH)(H₂O)](ClO₄)₂ (0.194 g, 0.40 mmol) was dissolved in a solution of sodium hydroxide (4 ml, 0.1 M). $(\text{NH}_4)_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$ (0.068 g, 0.20 mmol) was added slowly, and the pH of the solution was adjusted to 8–8.5 by means of a solution of sodium hydroxide (2 M). The mixture was set aside in a stoppered flask. After a few days, red, elongated crystals had separated. The crystals were filtered and washed with a solution of sodium perchlorate (1 M) and with ethanol (75%). Yield: 0.098 g (94%). Anal. Calcd. for [MoO₄Cr(C₁₀H₂₄N₄)₂](ClO₄)₂·H₂O: Mo 18.42, Cr 9.99, C 23.07, H 4.84, N 10.76, Cl 6.81. Found: Mo 17.01, Cr 9.92, C 23.15, H 4.87, N 10.63, Cl 6.95. In other cases the compound did not contain crystal water. (λ,ε) = (519,266), (390,142), (280sh,2544), (205,41739).

Exactly the same compound could be synthesized by an identical procedure from compounds containing molybdenum in a lower oxidation state, such as $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ or $2\text{HCl}[\text{Mo}_6\text{Cl}_8]\text{Cl}_4\cdot 8\text{H}_2\text{O}$. In both cases the yields were considerably lower, but the

crystals were larger and suitable for structure determination.

$\{[\text{MoO}_4\text{Crcyclam}]_2\}I_2$ (**1a**) This compound was synthesized exactly as described for **1**, but from *cis*-[Crcyclam(OH)(H₂O)]I₂·2H₂O (0.184 g, 0.32 mmol) and $(\text{NH}_4)_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$ (0.051 g, 0.15 mmol). The crystals were washed with ethanol (96%). Yield: 0.063 g (78%). Anal. Calcd. for [MoO₄Cr(C₁₀H₂₄N₄)₂]I₂: Mo 17.79, Cr 9.64, C 22.28, H 4.49, N 10.39, I 23.54. Found: Mo 18.19, Cr 9.38, C 22.20, H 4.64, N 10.33, I 23.74. (λ,ε) = (519,266), (390,154).

$\{[\text{MoO}_4\text{Rhcyclam}]_2\}(\text{ClO}_4)_2$ (**2**) *cis*-[Rhcyclam(H₂O)₂](CF₃SO₃)₃ 0.160 g (0.20 mmol) was dissolved in a solution of sodium hydroxide (2 ml, 0.1 M). $(\text{NH}_4)_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$ (0.051 g, 0.15 mmol) was added, and the pH of the solution was adjusted to 8–8.5 by means of a solution of sodium hydroxide (1 M). A solution of sodium perchlorate (1 ml, 1 M) was added and the suspension was set aside in a stoppered flask. After three days yellow crystals had separated. They were washed with sodium perchlorate (1 M) and with ethanol (75%). Yield: 0.078 g (92%). Anal. Calcd. for [MoO₄Rh(C₁₀H₂₄N₄)₂](ClO₄)₂: C 21.35, H 4.30, N 9.96, Cl 6.30. Found: C 21.18, H 4.46, N 9.85, Cl 6.41. (λ,ε) = (343,752), (290sh,2800), (194,64838).

$\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4\cdot 6\text{H}_2\text{O}$ (**3**) This compound was synthesized exactly as described for **1**, but from *cis*-[Crcyclam(OH)(H₂O)](ClO₄)₂ (0.194 g, 0.40 mmol) and K_2WCl_6 (0.142 g, 0.30 mmol). After 2 weeks large, compact, violet crystals had separated. They were filtered and washed as described before. Yield: 0.079 g (43%). Anal. Calcd. for [WO₄Cr(C₁₀H₂₄N₄)₄](ClO₄)₄·6H₂O: C 19.17, H 4.34, N 8.94, Cl 5.65. Found: C 19.20, H 4.50, N 8.97, Cl 5.72. The complex readily lost more or less of the crystal water. (λ,ε) = (527,400), (380,444), (300sh,3257), (211,58404).

$\{[\text{WO}_4\text{Crcyclam}]_2\}I_2\cdot 8\text{H}_2\text{O}$ (**3a**) This compound was synthesized exactly as described for **3**, but from *cis*-[Crcyclam(OH)(H₂O)]I₂·2H₂O (0.231 g, 0.40 mmol) and K_2WCl_6 (0.142 g, 0.30 mmol). The crystals that separated after a few days were washed with ethanol (96%). Yield: 0.084 g (60%). Anal. Calcd. for [WO₄Cr(C₁₀H₂₄N₄)₂]I₂·8H₂O: W 26.30, Cr 7.44, C 17.18, H 4.61, N 8.01, I 18.15. Found: W 27.20, Cr 7.32, C 17.34, H 3.75, N 8.01, I 18.40. (λ,ε) = (519,260), (389,284).

Analyses. The chromium analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer. The contents of molybdenum and tungsten were determined by spectrophotometric methods involving thiocyanato complexes. The carbon, hydrogen and nitrogen analyses were carried out at the microanalytical laboratory of the H.C. Ørsted Institute using standard methods.

Optical spectroscopy. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 17 spectrophotometer. The spectra are characterized above by their maxima (λ, ϵ), where λ is in nm and the molar absorption coefficient ϵ is in units of $\text{l mol}^{-1} \text{cm}^{-1}$. In Fig. 4, however, the absorption coefficient is in units of $\text{l mol}_{\text{Cr}}^{-1} \text{cm}^{-1}$ to facilitate comparison. The compounds were dissolved in water.

Magnetic susceptibility measurements. The magnetic susceptibilities (cgs units) of powdered samples were measured by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T. The cgs unit ($\text{cm}^3 \text{mol}^{-1}$) can be converted to the SI unit ($\text{m}^3 \text{mol}^{-1}$) by multiplying the ordinate value by $4\pi \times 10^{-6}$. The susceptibility data have been corrected for diamagnetism by Pascal's constants. A more detailed description of the equipment is published elsewhere.⁸

Crystal structure determinations. Cell dimensions were determined from reflections measured at 4 positions:

$2\theta, \omega, \chi, \phi$; $-2\theta, -\omega, \chi, \phi$; $2\theta, \omega, 180 + \chi, \phi$ and $-2\theta, -\omega, 180 + \chi, \phi$. Intensities were measured at room temperature using a Huber diffractometer. Nb-filtered $\text{MoK}\alpha$ radiation was used for **1** and **3**, graphite-monochromatized $\text{MoK}\alpha$ radiation for **2**. The intensities of two standard reflections were measured every 50 reflexions. Crystal data are given in Table 1.

Data were corrected for background, Lorentz and polarization effects and for absorption. Structures of **1** and **3** were determined using MULTAN80⁹ and subsequent difference electron density maps. For the Mo–Cr dimer the hydrogen atoms of the ligands were included at the calculated positions. The structures were refined by the least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ using a modification of ORFLS.¹⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. The perchlorate ions in **3** were highly disordered, and so were treated as free rotors. The largest peak on the final difference map is 1.4 Å from Cl(1).

The Mo–Rh dimer was refined using the coordinates of the isomorphous Mo–Cr compound as starting values.

Table 1. Crystal data for $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ (**1**), $\{[\text{MoO}_4\text{Rhyclam}]_2\}(\text{ClO}_4)_2$ (**2**), and $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ (**3**).

Compound	1	2	3
FW/g mol ⁻¹	1023.38	1125.20	2404.07
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcn</i>
Cell parameters (295 K)			
<i>a</i> /Å	10.051(1)	9.858(2)	19.572(2)
<i>b</i> /Å	15.162(2)	15.269(2)	24.347(4)
<i>c</i> /Å	12.244(1)	12.373(2)	16.601(2)
β /°	104.001(8)	105.203(9)	
<i>V</i> /Å ³	1810.5(3)	1797.1(4)	7911(2)
No. of reflexions centred	4 × 30	4 × 30	4 × 30
2 θ range/°	17.1–28.7	26.2–30.0	15.2–27.8
Calculated density (295 K)/g cm ⁻³	1.877	2.079	2.018
Formula units per cell	2	2	4
Crystal size/mm ³	0.10 × 0.11 × 0.44	0.31 × 0.34 × 0.50	0.13 × 0.23 × 0.30
Development forms	{011}, {411}, {211}	{011} {302}	{010}, {110}, {100}
Radiation (MoK α) λ /Å	0.71073	0.71073	0.71073
Filter	Nb		Nb
Monochromator		Graphite	
Linear absorption coefficient μ /cm ⁻¹	14.55	17.81	66.54
Range of transmission factors	0.838–0.886	0.545–0.659	0.284–0.410
Scan type	ω -2 θ	ω -2 θ	ω -2 θ
ω -Scan width $\Delta\theta$ /°	0.80 + 0.346tan θ	1.4 + 0.346tan θ	1.0 + 0.346tan θ
No. of steps	50	50	50
Time per step/s	2	1	2
Θ -limits/°	1.0–27.5	1.0–30.0	1.0–22.5
Octants collected	<i>hk</i> ± <i>l</i>	± <i>hk</i> ± <i>l</i>	<i>hk</i> ± <i>l</i>
<i>R</i> _{int}	0.018	0.018	0.018
Standard reflexions	0 8 0, 2 2 $\bar{7}$	0 6 0, 4 0 $\bar{2}$	0 10 0, 4 0 0
Fall-off in intensity (%)	< 1	< 1	7
No. of unique data	4162	5218	5231
No. of data with $I/\sigma(I) > 3.0$	2113	4070	2454
No. of variables	227	251	410
Weights, $w^{-1} = [\sigma_{\text{cs}}(F^2) + (1.0 + A) \cdot F^2]^{1/2} - F $			
<i>A</i>	0.02	0.03	0.03
$R = \sum(F_o - F_c) / \sum F_o $	0.064	0.036	0.054
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.080	0.058	0.066
<i>S</i>	2.04	1.75	1.55
$\Delta/\sigma_{\text{max}}$	0.36	0.29	0.16
$\Delta\rho_{\text{max}}/e \text{ \AA}^{-3}$	1.3(2)	1.5(1)	3.4(2)

Table 2. $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ fractional coordinates and equivalent isotropic thermal parameters in \AA^2 .

Atom	x	y	z	U_{eq}^a
Mo	0.1491(1)	0.6125(1)	0.0700(1)	0.037(1)
Cr	0.1739(2)	0.3867(1)	0.1513(1)	0.025(1)
Cl	-0.3544(5)	0.0957(2)	0.2159(3)	0.070(3)
O(1)	0.0100(8)	0.3915(4)	0.0324(5)	0.040(4)
O(2)	0.1913(8)	0.5137(4)	0.1462(6)	0.045(5)
O(3)	0.2771(9)	0.6370(6)	0.0068(7)	0.064(6)
O(4)	0.1389(9)	0.6980(5)	0.1617(6)	0.055(5)
O(5)	-0.4836(13)	0.0814(8)	0.1386(9)	0.109(9)
O(6)	-0.3536(13)	0.0453(8)	0.3140(8)	0.116(9)
O(7)	-0.3421(13)	0.1845(8)	0.2403(14)	0.150(12)
O(8)	-0.2509(14)	0.0645(9)	0.1751(10)	0.128(11)
N(1)	0.0690(11)	0.3978(6)	0.2783(8)	0.051(7)
C(2)	0.1686(20)	0.3915(11)	0.3876(10)	0.084(11)
C(3)	0.3048(19)	0.4330(8)	0.3791(10)	0.068(10)
N(4)	0.3456(11)	0.3898(6)	0.2875(8)	0.055(6)
C(5)	0.4686(16)	0.4352(8)	0.2725(14)	0.079(10)
C(6)	0.5163(15)	0.3970(10)	0.1685(13)	0.076(11)
C(7)	0.4261(16)	0.4105(9)	0.0622(14)	0.072(11)
N(8)	0.2947(12)	0.3609(7)	0.0397(7)	0.054(7)
C(9)	0.3113(18)	0.2660(10)	0.0304(11)	0.076(11)
C(10)	0.1826(16)	0.2172(9)	0.0421(12)	0.067(10)
N(11)	0.1511(11)	0.2501(6)	0.1509(8)	0.055(7)
C(12)	0.0207(16)	0.2123(8)	0.1571(12)	0.071(10)
C(13)	-0.0141(16)	0.2438(11)	0.2639(13)	0.080(11)
C(14)	-0.0474(18)	0.3399(11)	0.2712(12)	0.082(12)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Hydrogen atoms were located from a difference map, but were kept fixed at calculated positions.

The atomic scattering factors were from Ref. 11, as were the anomalous scattering corrections for Cr, Mo, Rh and W.

Results and discussion

Synthetic aspects. We have earlier demonstrated the ability of *cis*- β -[Crbispietn(OH)₂]⁺ or corresponding complex ions to act as chelate, bidentate ligands to bivalent or trivalent ions.¹²⁻¹⁷ An attempt¹ to make a complex with molybdenum(III) as central atom, however, resulted in an octanuclear complex with a cubane core of Mo^{VI}₄O₈⁸⁺. It was possible to synthesize a corresponding complex with a cubane core of W^{VI}₄O₈⁸⁺. In this experiment we have replaced *cis*- β -[Crbispietn(OH)(H₂O)](ClO₄)₂ by *cis*-[Crcyclam(OH)(H₂O)](ClO₄)₂. This change lead to the formation of two different types of bimetallic complexes, namely a octanuclear complex of the above-mentioned type with tungsten and a tetranuclear complex with molybdenum. The last complex is related to a dimeric iron(III) complex with three bridges of molybdate(VI),¹⁸ but contains only two bridges of molybdate(VI).

When the complexes were isolated as iodide salts, they both seem to come out as tetranuclear complexes. Chromium(III) could be replaced by rhodium(III) but not by cobalt(III), because the rearrangement of *cis*-[Cocyclam(OH)₂]⁺ to *trans*-[Cocyclam(OH)₂]⁺ was too fast. All complexes were soluble and relatively stable in water and

Table 3. $\{[\text{MoO}_4\text{Rhyclam}]_2\}(\text{ClO}_4)_2$ fractional coordinates and equivalent isotropic thermal parameters in \AA^2 .

Atom	x	y	z	U_{eq}^a
Mo	0.14474(4)	0.61265(2)	0.07551(3)	0.0314(2)
Rh	0.18462(3)	0.38705(2)	0.16046(2)	0.0210(2)
Cl	-0.35870(16)	0.10111(9)	0.21516(14)	0.0603(8)
O(1)	0.0178(3)	0.3968(2)	0.0280(3)	0.045(2)
O(2)	0.1942(3)	0.5200(2)	0.1652(3)	0.045(2)
O(3)	0.2739(5)	0.6306(3)	0.0081(4)	0.070(3)
O(4)	0.1373(4)	0.7055(2)	0.1570(3)	0.045(2)
O(5)	-0.4918(6)	0.0873(4)	0.1362(5)	0.094(4)
O(6)	-0.3540(6)	0.0502(4)	0.3134(4)	0.094(4)
O(7)	-0.3453(6)	0.1897(3)	0.2471(6)	0.112(4)
O(8)	-0.2471(6)	0.0745(4)	0.1702(5)	0.103(4)
N(1)	0.0692(5)	0.3984(3)	0.2765(3)	0.048(2)
C(2)	0.1659(9)	0.3913(4)	0.3937(5)	0.068(4)
C(3)	0.3027(7)	0.4308(3)	0.3905(4)	0.063(3)
N(4)	0.3525(4)	0.3889(2)	0.2993(3)	0.042(2)
C(5)	0.4772(6)	0.4354(3)	0.2841(6)	0.076(4)
C(6)	0.5316(6)	0.4012(4)	0.1862(7)	0.075(4)
C(7)	0.4364(7)	0.4180(5)	0.0712(7)	0.078(5)
N(8)	0.3049(5)	0.3704(3)	0.0480(4)	0.052(3)
C(9)	0.3247(7)	0.2732(4)	0.0329(5)	0.066(4)
C(10)	0.1982(7)	0.2269(3)	0.0412(5)	0.061(3)
N(11)	0.1673(4)	0.2538(2)	0.1490(3)	0.044(2)
C(12)	0.0287(6)	0.2175(3)	0.1553(5)	0.065(3)
C(13)	-0.0132(6)	0.2456(4)	0.2594(6)	0.072(4)
C(14)	-0.0512(6)	0.3407(5)	0.2641(6)	0.075(4)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

N-methylformamide, but the complexes were remarkably insoluble in water compared with the earlier described complexes with bispictn.

Description of structures. $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ and $\{[\text{MoO}_4\text{Rhyclam}]_2\}(\text{ClO}_4)_2$ are isostructural. They are both dimers, and the cations are centrosymmetric and contain eight-membered $(\text{Mo}-\text{O}-\text{M}-\text{O})_2$ rings (Fig. 1) which are almost planar. Deviations from planarity are from 0.03 to 0.11 Å for **1** and from 0.07 to 0.17 Å for **2**. The molybdenum atoms are tetrahedrally coordinated to four oxygen atoms; the Mo–O distances within the ring are 1.763(6) and 1.779(7) Å for **1** and 1.775(3) and 1.785(3) Å for **2**. The exocyclic Mo–O distances are somewhat shorter, 1.694(8) and 1.734(7) Å for **1** and 1.717(4) and 1.753(3) Å for **2**. Strain within the rings causes an opening of the O–Mo–O angle to 113.8(3)° for **1** and 115.6(1)° for **2**; there is, however, no opening of the O–Cr–O or O–Rh–O angles. Mo–O–M angles are 174.0(4) and 148.3(4)° for **1** and 167.9(1) and 140.4(1)° for **2**. Rh–O and Rh–N distances are close to those expected, 2.011(5) and 2.058(3) Å, from the Cambridge Structural Database (CSD).¹⁹ Cr–O and Cr–N do not agree as well with the CSD values of 1.964(1) and 2.060(2) Å; in particular, the Cr–O distance of 1.927(9) Å is much shorter than expected.

$\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ is tetrameric. The cation (Fig. 2) has exact two-fold symmetry through Cr(2)

and Cr(3), and is built up about a distorted cube of tungsten and oxygen atoms (Fig. 3) similar to that in $\{[\text{MoO}_4\text{Crbispictn}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$.¹ There are four chemically distinct tungsten–oxygen distances. The mean values for these are: $\text{W}-\text{O}_t = 1.71(2)$ Å, $\text{W}-\text{O}_b = 2.23(2)$ Å, $\text{W}-\text{O}_c = 1.83(1)$ Å and $\text{W}-\text{O}_d = 2.06(1)$ Å (*t* = terminal, *b* = bridge oxygen trans to O_t , *c* = bonded to Cr, *d* = bridge oxygen trans to O_c). The internal O–W–O angles have a mean value of 73.3(3)° and the external ones 101.3(6)°; angles involving only one W–O within the cube are closer to right angles, $\text{O}-\text{W}-\text{O}_c = 88.4(11)^\circ$ and $\text{O}-\text{W}-\text{O}_t = 96.2(12)^\circ$. Angles at the oxygen atoms are $\text{W}-\text{O}-\text{W}$ 104.5(4)° and $\text{W}-\text{O}-\text{Cr} = 146.6(6)^\circ$. Cr–O is 1.90(1) Å and Cr–N is 2.07(1) Å. There is one short W–W distance, 3.270(2) Å, and two long ones, 3.392(2) Å. The acute O–W–O angles indicate that there is no metal–metal bonding,²⁰ which is consistent with a closed-shell metal configuration.

The cyclam ligand in all three complexes has the folded configuration (designated V by Bosnich *et al.*²¹) in which alternate amine hydrogen atoms are on opposite sides of the macrocyclic ring. The five- and six-membered rings have *gauche* and *chair* conformations, respectively. The four chiral nitrogen atoms of the ligand have identical chirality. In the dimers one cyclam is *R,R,R,R* and the other *S,S,S,S*, whereas in the tetramer all nitrogen atoms are *R* in one cation and *S* in the centrosymmetrically related one.

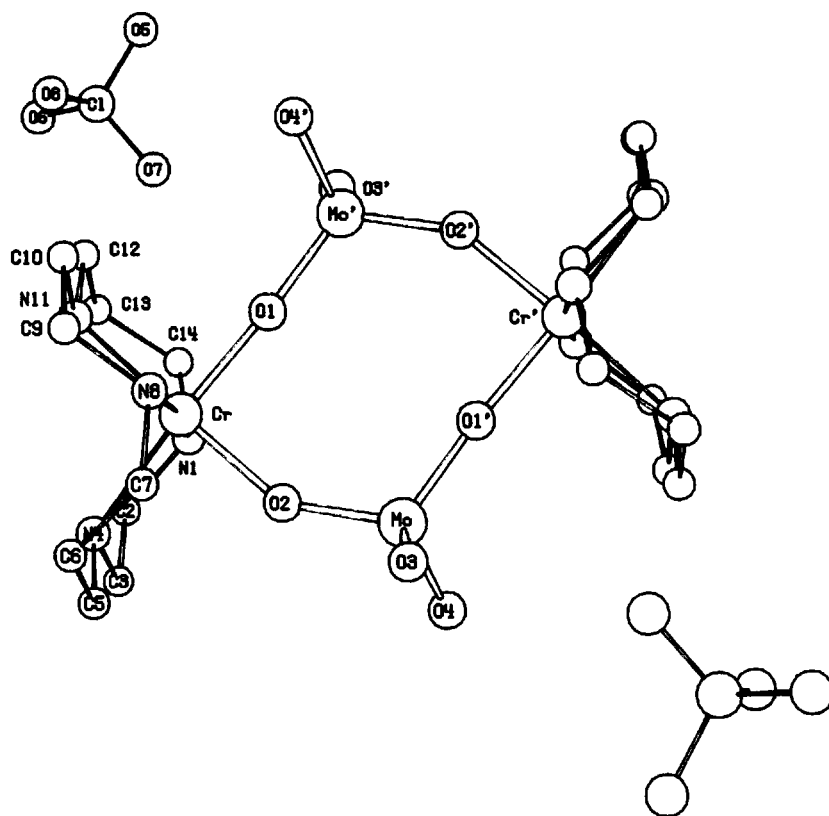


Fig. 1. A perspective view of $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$.

Table 4. $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ and equivalent isotropic thermal parameters in \AA^2 .

Atom	x	y	z	U_{eq}^a
W(1)	-0.0277(1)	0.1445(1)	0.1533(1)	0.035(1)
W(2)	0.0797(1)	0.2397(1)	0.2105(1)	0.039(1)
Cr(1)	0.1987(2)	0.1935(2)	0.3593(3)	0.043(3)
Cr(2)	0.0000	0.3688(3)	0.2500	0.61(6)
Cr(3)	0.0000	0.0153(3)	0.2500	0.038(4)
O(1)	0.0604(9)	0.1578(7)	0.2205(13)	0.153(17)
O(2)	-0.0194(9)	0.2286(7)	0.1753(12)	0.046(14)
O(3)	0.1532(9)	0.2361(8)	0.2777(13)	0.052(14)
O(4)	-0.1174(10)	0.1506(8)	0.1292(12)	0.050(14)
O(5)	0.1174(10)	0.2361(9)	0.1174(13)	0.055(15)
O(6)	-0.0082(10)	0.1501(8)	0.4405(12)	0.056(15)
O(7)	-0.00239(11)	0.0703(7)	0.1752(12)	0.050(14)
O(8)	0.0603(10)	0.3135(7)	0.2168(15)	0.063(15)
N(1)	0.2791(14)	0.2499(13)	0.3567(23)	0.080(24)
C(2)	0.2554(29)	0.2979(19)	0.4039(47)	0.153(56)
C(3)	0.2211(28)	0.2839(23)	0.4831(40)	0.150(56)
N(4)	0.1680(17)	0.2415(12)	0.4546(21)	0.081(25)
C(5)	0.1439(23)	0.2103(19)	0.5257(26)	0.087(33)
C(6)	0.1955(23)	0.1731(20)	0.5655(27)	0.099(36)
C(7)	0.2132(26)	0.1237(17)	0.5101(29)	0.104(38)
N(8)	0.2472(14)	0.1411(11)	0.4382(15)	0.050(19)
C(9)	0.2644(19)	0.0901(13)	0.3948(22)	0.061(26)
C(10)	0.2962(22)	0.1059(15)	0.3135(26)	0.086(32)
N(11)	0.2449(15)	0.1465(10)	0.2750(18)	0.067(21)
C(12)	0.2860(22)	0.1753(17)	0.2069(24)	0.092(33)
C(13)	0.3358(20)	0.2191(19)	0.2372(29)	0.087(34)
C(14)	0.3054(25)	0.2656(19)	0.2785(28)	0.096(36)
N(15)	-0.0436(17)	0.3773(12)	0.1361(24)	0.094(27)
C(16)	-0.0014(35)	0.4234(22)	0.0943(42)	0.151(53)
C(17)	0.0714(40)	0.4255(23)	0.1199(49)	0.153(59)
N(18)	0.0707(18)	0.4260(12)	0.2048(28)	0.086(26)
C(19)	0.1376(24)	0.4199(17)	0.2418(35)	0.087(34)
C(20)	0.1477(46)	0.4240(23)	0.3156(48)	0.187(77)
C(21)	0.1133(39)	0.3806(34)	0.3693(49)	0.204(83)
N(22)	-0.0956(12)	0.0069(11)	0.2922(18)	0.055(19)
C(23)	-0.1054(22)	-0.0374(19)	0.3512(26)	0.103(36)
C(24)	-0.0384(24)	-0.0392(15)	0.4013(24)	0.084(30)
N(25)	0.0226(17)	-0.0426(10)	0.3407(18)	0.061(19)
C(26)	0.0847(27)	-0.0361(15)	0.3875(25)	0.091(33)
C(27)	0.1455(20)	-0.0393(16)	0.3273(26)	0.068(29)
C(28)	0.1564(25)	0.0024(22)	0.2673(30)	0.114(43)
Cl(1)	0.2907(7)	0.0380(4)	0.0438(7)	0.110(10)
Cl(2)	0.5000	0.3162(7)	0.2500	0.157(19)
Cl(3)	0.5000	0.0742(8)	0.2500	0.270(33)
H ₂ O(1)	0.0331(19)	0.2853(15)	0.4632(23)	0.176(36)
H ₂ O(2)	0.1604(15)	0.1014(13)	0.1337(30)	0.179(36)
H ₂ O(3)	0.3780(19)	0.1944(16)	0.4823(24)	0.185(39)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Electronic spectra. The electronic spectra (visible region) of the three different complexes with chromium dissolved in water are shown in Fig. 4. $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4$ has a spectrum, $(\lambda, \epsilon/4) = (527, 100)$, $(380\text{sh}, 111)$, with a great likeness to the spectrum of the corresponding complex with bispictn, $(\lambda, \epsilon/4) = (522, 106)$, $(380\text{sh}, 155)$.¹ In both cases the second band in the d-d region of chromium(III) is overlapped by a charge-transfer band.

The spectra of $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ and the complex alleged to be $\{[\text{WO}_4\text{Crcyclam}]_2\}\text{I}_2$ are both characterized by two distinct bands, $(\lambda, \epsilon/2)_{\text{Mo}} = (519, 133)$, $(390, 71)$ and $(\lambda/\epsilon/2)_{\text{W}} = (519, 130)$, $(389, 142)$.

Although there is a great likeness in shape and positions of the first bands, there is a greater overlap from the charge-transfer band in the tungsten complex.

Magnetic susceptibility. The temperature dependence of the magnetic susceptibility (in cgs units) of $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$, was measured in the temperature range 4–300 K as shown in Fig. 5. The susceptibility shows a maximum at approximately 29.4 K, and the effective magnetic moment declines from $7.5\mu_{\text{B}}$ at room temperature to $1.6\mu_{\text{B}}$ at 4 K. These data are quite similar to those obtained for the similar Mo and W complexes with the ligand bispictn reported earlier.¹

Table 5. $\{[\text{MoO}_4\text{Crcyclam}]_2\}(\text{ClO}_4)_2$ Selected bond distances (in Å) and angles (in °).

	Range	<i>n</i>	Mean ^a
Mo—Mo	4.592(2)	1	4.592(2)
Mo—O	1.694(8)–1.779(7)	4	1.743(19)
Mo—O in ring	1.763(6)–1.779(7)	2	1.771(8)
Mo—O term.	1.694(8)–1.734(7)	2	1.714(20)
Cr—O	1.918(7)–1.936(7)	2	1.927(9)
Cr—N	2.072(10)–2.090(9)	4	2.083(4)
O—Mo—O in ring	113.8(3)	1	113.8(3)
O—Mo—O	107.3(3)–109.8(3)	5	108.6(5)
O—Cr—O	90.3(3)	1	90.3(3)
O—Cr—N cis	86.5(3)–93.8(4)	6	91.1(14)
O—Cr—N trans	175.2(4)–178.0(3)	2	176.6(14)
N—Cr—N trans	171.5(4)	1	171.5(4)
N—Cr—N 5-ring	82.7(4)–83.9(4)	2	83.3(6)
N—Cr—N 6-ring	90.4(4)–91.6(4)	2	91.0(4)
N—Cr—N no-ring	95.4(4)	1	95.4(4)
Mo'—O(1)—Cr	174.0(4)	1	174.0(4)
Mo—O(2)—Cr	148.3(4)	1	148.3(4)

^a Standard deviation of mean = $[\sum(x-\bar{x})^2]^{1/2}/n(n-1)$.

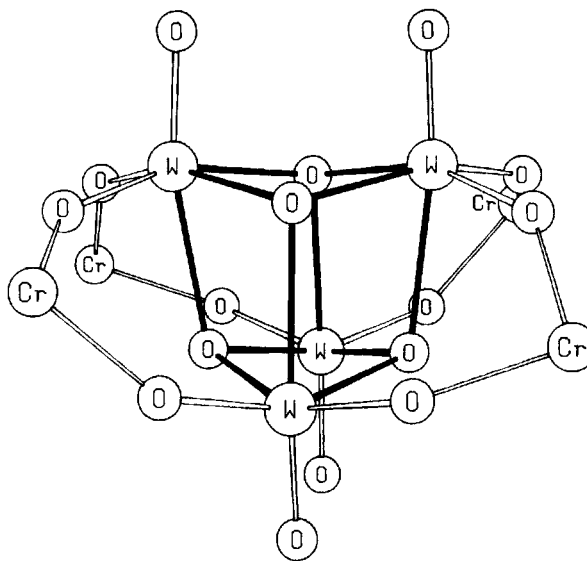


Fig. 3. A perspective view of the W_4O_4 cube.

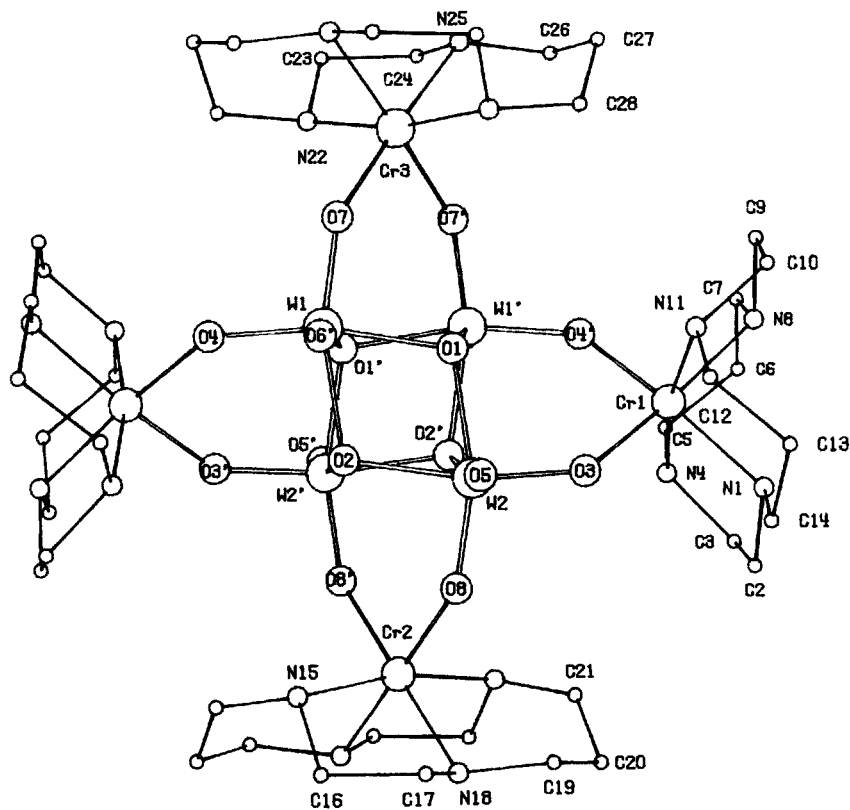


Fig. 2. A perspective view of the $[\text{WO}_4\text{Crcyclam}]_4^{4+}$ cation.

Table 6. $\{[\text{MoO}_4\text{Rhcyclam}]_2\}(\text{ClO}_4)_2$ Selected bond distances (in Å) and angles (in °).

	Range	<i>n</i>	Mean ^a
Mo–Mo	4.547(1)	1	4.547(1)
Mo–O	1.717(4)–1.785(3)	4	1.758(15)
Mo–O in ring	1.775(3)–1.785(3)	2	1.780(5)
Mo–O term.	1.717(4)–1.753(3)	2	1.735(18)
Rh–O	2.000(3)–2.032(3)	2	2.016(16)
Rh–N	2.043(3)–2.066(4)	4	2.054(5)
O–Mo–O in ring	115.6(1)	1	115.6(1)
O–Mo–O	107.3(2)–109.2(2)	5	108.2(3)
O–Rh–O	88.3(1)	1	88.3(1)
O–Rh–N cis	85.8(2)–96.4(2)	6	89.9(18)
O–Rh–N trans	174.7(1)–177.3(1)	2	176.0(13)
N–Rh–N trans	177.2(1)	1	177.2(1)
N–Rh–N 5-ring	83.3(2)–83.5(2)	2	83.4(1)
N–Rh–N 6-ring	94.6(2)–95.0(2)	2	94.8(2)
N–Rh–N no-ring	96.1(1)	1	96.1(1)
Mo'–O(1)–Rh	167.9(1)	1	167.9(1)
Mo–O(2)–Rh	140.4(1)	1	140.4(1)

^a Standard deviation of mean = $[\sum(x-\bar{x})^2]^{1/2}/n/(n-1)$.

The temperature dependence of the magnetic susceptibilities $\chi'_{\text{mol,exp}}$ were approximated by eqn. (1)²¹

$$\chi'_{\text{mol,exp}} \approx \chi'_{\text{mol,calc}}$$

$$= \frac{N \sum_i \frac{\partial E_i}{\partial B} \exp(-E_i/kT)}{B \sum_i \exp(-E_i/kT)} + K + C/T \quad (1)$$

by minimization of eqn. (2)

$$\sum_T \frac{[\chi'_{\text{mol,exp}}(T) - \chi'_{\text{mol,calc}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial \chi'}{\partial T}\right)^2 \sigma^2(T)} \quad (2)$$

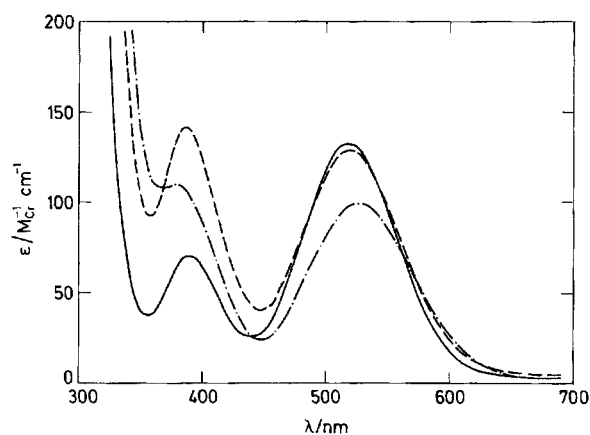


Fig. 4. The absorption spectra (visible region) of $[\text{MoO}_4\text{Crcyclam}]_2^{2+}$ (—), $[\text{WO}_4\text{Crcyclam}]_2^{2+}$ (---) and $[\text{WO}_4\text{Crcyclam}]_4^{4+}$ (-·-·-). The absorption coefficients are depicted in units of $M_{\text{Cr}}^{-1} \text{cm}^{-1}$ to facilitate a comparison.

Table 7. $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ selected interatomic distances (in Å) and angles (in °), t=terminal W–O, b=bridge O trans to t, c=O bonded to Cr, d=bridge O trans to c, *n*=number of chemically equivalent bonds or angles.

	Range	<i>n</i>	Mean ^a
W–W short	3.270(2)	1	3.270(2)
W–W long	3.390(3)–3.394(2)	2	3.392(2)
W–O t	1.71(2)–1.71(2)	2	1.71(0)
W–O b	2.21(2)–2.25(2)	2	2.23(2)
W–O c	1.81(2)–1.85(2)	4	1.83(1)
W–O d	2.04(2)–2.09(2)	4	2.06(1)
Cr–O	1.87(2)–1.92(2)	4	1.90(1)
Cr–N	2.01(2)–2.11(3)	8	2.07(1)
O–W–O dd, bd	71.9(7)–74.2(9)	6	73.3(3)
O–W–O ct	101.0(10)–103.9(9)	4	102.0(7)
O–W–O cc	99.5(10)–100.0(10)	2	99.8(3)
O–W–O tb	165.1(8)–168.3(8)	2	166.7(16)
O–W–O cd	155.8(8)–157.5(8)	4	156.5(4)
O–W–O td	92.8(9)–98.3(9)	4	96.2(12)
O–W–O bc	83.8(8)–88.2(7)	4	86.2(10)
O–W–O cd	87.1(8)–92.8(8)	4	90.6(13)
W–O–W dd, bd	103.0(8)–105.9(8)	6	104.5(4)
W–O–Cr	145.2(11)–148.1(12)	4	146.6(6)
O–Cr–O	88.1(12)–89.5(12)	3	88.8(4)
O–Cr–N cis	87.2(10)–97.6(10)	12	91.9(10)
O–Cr–N trans	171.0(12)–175.5(10)	3	173.8(10)
N–Cr–N 5-ring	82.1(14)–83.3(10)	4	82.9(3)
N–Cr–N 6-ring	89.2(12)–91.2(13)	4	89.9(4)
N–Cr–N no-ring	94.2(12)–97.0(20)	3	95.8(8)
N–Cr–N trans	168.4(15)–170.0(13)	3	169.0(5)

^a Standard deviation of mean = $[\sum(x-\bar{x})^2]^{1/2}/n/(n-1)$.

within the framework of nonlinear regression analysis. $\sigma(\chi')$ and $\sigma(T)$ are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. In eqn. (1) C/T accounts for paramagnetic impurities, K accounts for temperature-independent para-

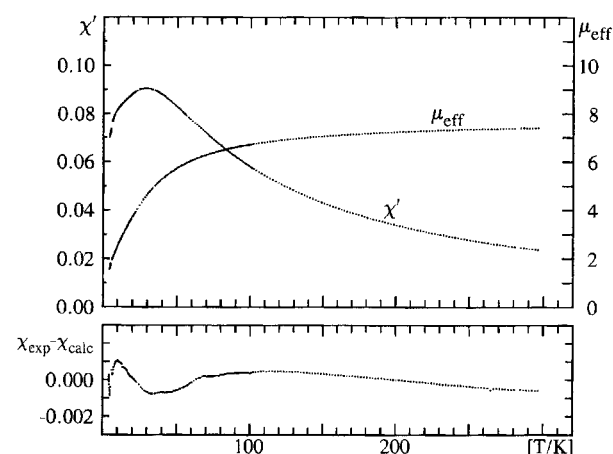


Fig. 5. The magnetic susceptibility (in cgs units) and the effective magnetic moment as a function of temperature for $\{[\text{WO}_4\text{Crcyclam}]_4\}(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$. The lower graph gives the difference between the measured and calculated susceptibilities with the parameters $g=1.98$ and $J=8.41 \text{ cm}^{-1}$ and $J'=-0.84 \text{ cm}^{-1}$.

magnetism and a minor deviation in the correction for diamagnetism. The energies E_i of the 256 components of the groundstate manifold for the tetranuclear chromium complex were obtained by means of the isotropic spin Hamilton operator, eqn. (3),

$$\hat{H} = \sum_{i=1}^4 g\mu_B \hat{S}_i \cdot \hat{H} + j \sum_{i=1}^4 \hat{S}_i \cdot \hat{S}_{(i+1) \bmod 4} + J' \sum_{i=1}^2 \hat{S}_i \cdot \hat{S}_{i+2} \quad (3)$$

where we have assumed that the g -values for the four chromium atoms are identical. The second term in eqn. (3) accounts for interactions between neighbouring chromium atoms, and the last term accounts for the interactions between opposite chromium atoms. The minimization resulted in the following parameters: $J = 8.41(5) \text{ cm}^{-1}$, $J' = -0.84(10) \text{ cm}^{-1}$, $g = 1.99$ and $C = 0.047$. This C -value can be interpreted as 7% mononuclear chromium(III) impurity or 2% of the tetranuclear chromium complex which has disintegrated. This was confirmed by the EPR spectrum at 4 K of a frozen glass of the complex dissolved in *N*-methylformamide. The only signal we could identify was from a mononuclear chromium(III) complex with a considerable zero-field splitting.²²

The apparent ferromagnetic interaction between the opposed chromium atoms may be a result of the Hamiltonian used in eqn. (3), where it has been assumed that the interaction between the different neighbouring chromium atoms are equivalent. However, this assumption is not dictated by the crystal structure, which only requires two interactions to be equal along the twofold axis, but simply because the Hamiltonian in eqn. (3) is easy to solve. A Hamiltonian as presented in eqn. (4),

$$\hat{H} = \sum_{i=1}^4 g\mu_B \hat{S}_i \cdot \hat{H} + \sum_{i=1}^4 J_{i(i+1)} \hat{S}_i \cdot \hat{S}_{(i+1) \bmod 4} + \sum_{i=1}^2 J'_{i(i+2)} \hat{S}_i \cdot \hat{S}_{i+2} \quad (4)$$

where the interactions between the neighbouring chromium atoms have different values, has not been used because it requires diagonalization of an 256×256 matrix for each step in the iteration procedure.

The magnetic susceptibility of $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}\text{I}_2$ are very alike. For the complex $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}\text{I}_2$ the susceptibility data are shown in Fig. 6. The magnetic moment decreases from $5.4\mu_B$ at room temperature to $3.1\mu_B$ at 4.2 K. This is the expected behaviour for a dinuclear chromium(III) complex with almost zero interaction. The obtained J -value of 2.09 cm^{-1} *vide infra* should give a maximum in the susceptibility curve at 4.4 K. This maximum has been hidden by susceptibility of the monomeric impurity. For the perchlorate salt the magnetic moment

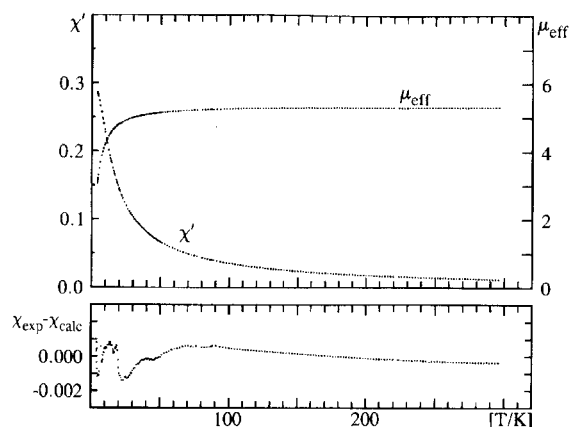


Fig. 6. The magnetic susceptibility (in cgs units) and the effective magnetic moment as a function of temperature for $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}\text{I}_2$. The lower graph gives the difference between the measured and calculated susceptibilities with the parameters $g = 1.98$ and $J = 2.09 \text{ cm}^{-1}$ and $D_1 = D_2 = 0.0095 \text{ cm}^{-1}$.

decreases from $5.4\mu_B$ at room temperature to $4.5\mu_B$ at 4.4 K.

For the dinuclear chromium complexes the energies E_i of the 16 levels of the ground state manifold were obtained from eqn. (5).

$$\hat{H} = \sum_{i=1}^2 g\mu_B \hat{S}_i \cdot \hat{H} + \sum_{i=1}^2 D_i \left[\hat{S}_{iz}^2 - \frac{1}{3} S_i(S_i + 1) \right] + J\hat{S}_1 \cdot \hat{S}_2 \quad (5)$$

Fitting the data for these almost non-interacting dinuclear chromium complexes to eqn. (1) necessitates one to put C equal to zero or keep it constant because J and C are strongly correlated. For the complex $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ the fitting gave $g = 1.98$, $J = 0.78 \text{ cm}^{-1}$, $D_1 = D_2 = -0.066 \text{ cm}^{-1}$, and for the complex $\{[\text{MoO}_4\text{Cr}(\text{cyclam})]_2\}\text{I}_2$ the fitting gave $g = 1.98$, $J = 2.09 \text{ cm}^{-1}$, $D_1 = D_2 = 0.0095 \text{ cm}^{-1}$.

Previously^{1,23-26} we have discussed the magnetic interactions through bonds (superexchange) in complexes with different nuclearities and different geometries. For the similar tetranuclear chromium(III) complexes¹ the important point was the non-orthogonality of the two sets of d-orbitals located on Mo or W, which were π -bonded via the p-orbitals on oxygens to the t_2 -orbitals on the chromium atoms. The interaction was expanded on the orbitals of the intervening atoms. In the present dinuclear chromium complexes the bridging molybdenum atoms are tetrahedrally coordinated, which means that the e-orbitals on molybdenum have to transmit the π -interactions between the two chromium atoms. However, these two e-orbitals are orthogonal or almost orthogonal when the metal is tetrahedrally coordinated, whereby the interactions vanish because the overlap integral between the two e-orbitals is zero or almost zero. For the perchlorate salt the O-Cr-O angle is 113.8° compared with the ideal tetrahedral angle of 109.47° . This result shows that J will

be small but not exactly zero, in accordance with the experiment.

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