Electronic Supplementary Material (ESI) for Chemical Society Reviews

Jahn-Teller Distortions in Transition Metal Compounds, and their Importance in Functional Molecular and Inorganic Materials

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Supporting Information

Table S1 Six-coordinate copper(II) compounds that have show unusual crystallographic coordination geometries, and the techniques used to demonstrate their true structure as a disordered (pseudo)-Jahn-Teller elongated octahedron. Only compounds for which these additional experiments have been done are included in the table.

	Crystallographic Cu site symmetry and apparent structural distortion from an ideal octahedral geometry	Ref.	Technique	Ref.
α-$M_2Pb[Cu(NO_2)_6]$ ($M^+ = K^+, Rb^+, Cs^+, Tl^+$)[a]	T_h, undistorted	1-3	TLS analysis VT powder and single crystal EPR EXAFS	4 5 6
β-$M_2Pb[Cu(NO_2)_6]$ ($M^+ = K^+, Rb^+, Cs^+, Tl^+$)[a]	D_{2h}, tetragonal compression	4, 7-9	TLS analysis VT powder and single crystal EPR Single crystal UV/vis EXAFS	4 5, 10-12 12 6
K_2CuF_4	D_{4h}, tetragonal compression	14	UV/vis and MCD measurements Susceptibility measurements Correction of incorrect space group	15 16 17
γ-$Cu_2(OH)_3Cl$, $[Cu(\mu_3\text{-}OH)_6]$ site	C_i, tetragonal compression	18	Reformulation of compound as $Cu_3(Cu_{1-x}Zn_x)(OH)_6Cl_2$ (x >0.5)	19
$[NH_4]_2[Cu(OH_2)_6][SO_4]_2$	C_i, small rhombic elongation	20	VT crystallography VT powder and single crystal EPR Comparative UV/vis and EPR spectra of other $M_2[Cu(OH_2)_6][SO_4]_2$ salts	21-24 21, 23 25, 26
$[Cu(pyO)_6]X_2$ ($X^- = BF_4^-, ClO_4^-, NO_3^-$)[b]	S_6, trigonal distortion	27-30	VT crystallography VT powder and single crystal EPR EXAFS	30 29, 31 32
$[Cu(en)_3]SO_4$	D_3, trigonal distortion	34	VT powder and single crystal EPR EXAFS VT crystallography	35 6 36
$[Cu(dien)_2][NO_3]_2$[c]	C_1, rhombical compression	37	VT crystallography and TLS analysis Single crystal UV/vis and EPR	38 39
$[Cu(terpy)_2]Br_2.3H_2O$, high-T phase[d]	C_1, rhombic compression	42	VT powder and single crystal EPR	42, 43
$[Cu(terpy)_2][PF_6]_2$, high-T phase[d]	S_4, tetragonal compression	44	VT powder and single crystal EPR	42
$[Cu(terpy)_2][BF_4]_2$[d]	C_1, rhombic compression	45	TLS analysis and VT powder EPR	45
$[Cu(1,1''\text{-dioxoterpy})_2][ClO_4]_2$	S_4, tetragonal compression	47	TLS analysis	47
$[Cu(1\text{-bpp})_2][BF_4]_2$	C_1, small rhombic elongation	48	VT crystallography and TLS analysis VT powder and single crystal EPR	49-51 50
β-$[Cu(1\text{-bpp}^{Mes})_2][ClO_4]_2.2CH_3NO_2$	C_1, small rhombic elongation	52	TLS analysis and VT powder EPR	52
$[Cu(\mu_3\text{-btz})_6(Cu\{CN\textit{t}Bu\})_4]$	S_4, tetragonal compression	53	VT powder EPR	53
$[Cu(tach)_2][NO_3]_2$[e]	C_{2h}, small tetragonal compression	54	VT powder and single crystal EPR	54
$[Cu(thch)_2][CH_3C_6H_4SO_3\text{-}4]_2$	C_i, rhombic compression	55	VT crystallography	55
$[H_3NC_6H_4Cl\text{-}3]_8[CuCl_6]Cl_4$	C_i, tetragonal compression	56	VT crystallography EXAFS VT powder and single crystal EPR Single crystal UV/vis EPR of Cu-doped Cd(II) analogue	57 58 59 59 60
$[Cu(ompa)_3][ClO_4]_2$	D_3, trigonal distortion	61	VT powder EPR Single crystal EPR	62 63
trans-$[Cu(O_2CCH_2OCH_3)_2(OH_2)_2]$	C_i, rhombic compression	64	VT crystallography	65
$[Cu(HC\{PPh_2O\}_3)_2][ClO_4]_2$	C_i, tetragonal compression	66	EXAFS VT crystallography and powder EPR	67 68
cis-$[Cu(vanillinate)(OH_2)_2]$	C_{2v},tetragonal compression	69	VT crystallography and TLS analysis	70
trans-$[Cu(O_2NO)_2(tmbim)_2]$	C_i, rhombic compression	71	TLS analysis	71
$[Cu([9]aneS_3)_2][BF_4]_2$	C_i, small tetragonal elongation	72	VT crystallography VT powder EPR and powder UV/vis EPR of Cu-doped Fe(II) analogue	73 73, 74 73

Table S1 continued.

	Crystallographic Cu site symmetry and apparent structural distortion from an ideal octahedral geometry	Ref.	Technique	Ref.
$[Cu([9]aneN_3)_2][Cu(CN)_3].2H_2O$[f]	C_1, small rhombic elongation	752	VT crystallography VT powder and single crystal EPR Powder UV/vis	75 74, 75 74
$[Cu(MeTRI)_2][BF_4]_2$	D_3, trigonal distortion	78	TLS analysis	78
$[Cu(NMe_3sar)][ClO_4]_4$	S_6, trigonal distortion	79	VT powder EPR EPR of Cu-doped Zn analogue	79 79
cis-$[Cu(ONO)(bipy)_2]NO_3$[g]	C_1, small rhombic elongation	80	VT crystallography	80
cis-$[Cu(hat)_2(OH_2)_2][ClO_4]_2$			VT powder EPR	82
$[Cu(\mu\text{-dpp})(OH_2)_2]_n[BF_4]_{2n}.2nH_2O$[h]	C_1, small rhombic elongation	83	VT crystallography	83
$[CuTp_2]$ (molecule B)[i]	C_i, small rhombic elongation	85	TLS analysis VT crystallography and powder EPR	85, 86 86
$[Cu(tpm)_2][NO_3]_2$	C_{3v}, trigonal distortion	87	EXAFS	87
$[Cu(tpp)_2]Br_2.8H_2O$	C_i, tetragonal compression	88	VT powder and single crystal EPR	88

[a]The γ-phase of the same compounds exhibits a crystallographically ordered rhombically elongated octahedral Cu(II) centre.[13] [b]The solvated forms of these materials, $[Cu(pyO)_6][NO_3]_2.2H_2O$ has a typical, static Jahn-Teller elongated geometry at 293 K.[33] [c]The salts $[Cu(dien)_2]Br_2$[40] and $[Cu(dien)_2]Cl[ClO_4]$[41] have a typical, static pseudo-Jahn-Teller elongated geometry at 293 K. [d]The salt $[Cu(terpy)_2][NO_3]_2$ has a typical, static pseudo-Jahn-Teller elongated geometry at 298 K.[46] [e]The salt $[Cu(tach)_2][ClO_4]_2$ has a typical, static Jahn-Teller elongated geometry at 293 K.[52] [f]The salts $[Cu([9]aneN_3)_2][ClO_4]_2$[76] and $[Cu([9]aneN_3)_2]Cl_2$[77] have a very similar, small rhombic elongated geometry at 293 K and so are also probably disordered although this was not studied. In contrast, $[Cu([9]aneN_3)_2][CF_3SO_4]_2.H_2O$ has a static Jahn-Teller elongation in the crystal.[77] [g]Several other fluxional complexes of type $[Cu(X)(bipy)_2]Y$, $[Cu(X)(phen)_2]Y$ or $[Cu(X)(bipyam)_2]Y$ ($X^- = NO_2^-$ or $MeCO_2^-$; $Y^- = NO_3^-$, BF_4^-, ClO_4^-, PF_6^- etc.) have also been studied by VT crystallography.[81] [h]The isomorphous ClO_4^- salt of the same compound also probably contains fluxional Cu centres, although this was not studied.[84] [i]There are two independent molecules in the crystal structure of this compound. The other molecule has a static Jahn-Teller elongated structure.

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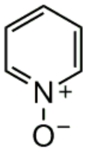
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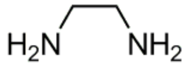
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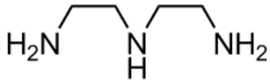
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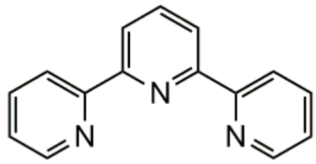
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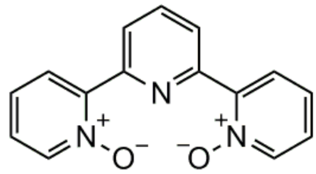
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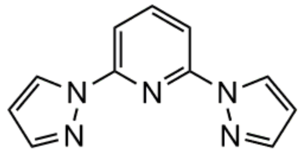
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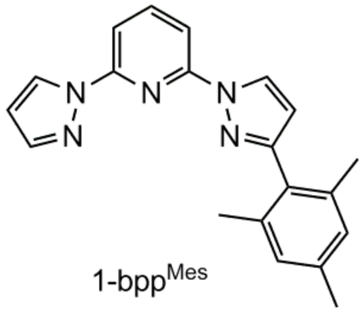
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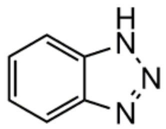
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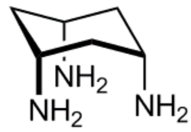
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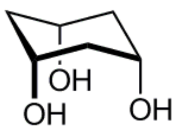
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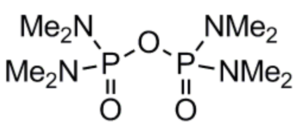
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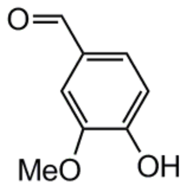
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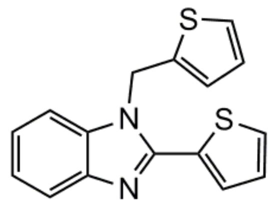
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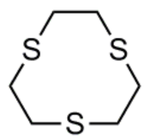
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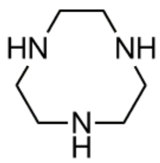
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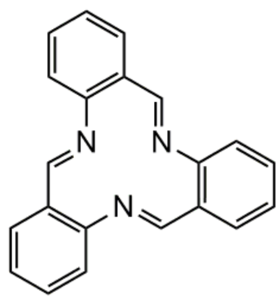
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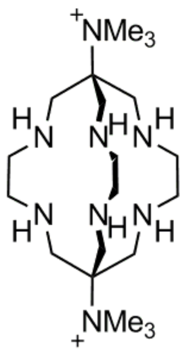
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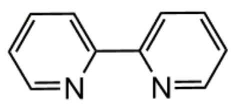
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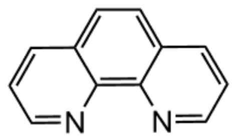
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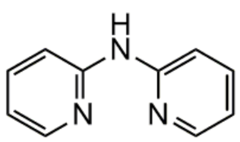
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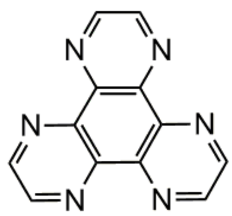
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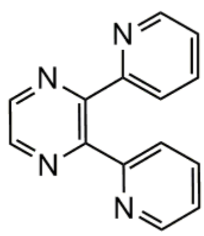
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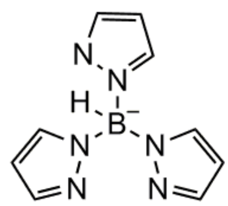
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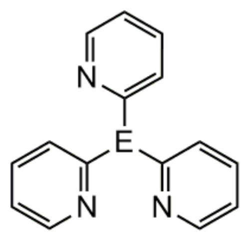
E = CH, tpm
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