

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

Malcolm A. Halcrow

*School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK
m.a.halcrow@leeds.ac.uk*

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 ₂ Pb[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 ₂ Pb[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 ₂ CuF 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) ₃ Cl, [Cu(μ_3 -OH) ₆] site	C _i , tetragonal compression	18	Reformulation of compound as Cu ₃ (Cu _{1-x} Zn _x)(OH) ₆ Cl 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 ₂ O, 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''-dioxoterypy) ₂][ClO ₄] ₂	S ₄ , tetragonal compression	47	TLS analysis	47
[Cu(1-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-bpp ^{Mes}) ₂][ClO ₄] ₂ ·2CH ₃ NO ₂	C ₁ , small rhombic elongation	52	TLS analysis and VT powder EPR	52
[Cu(μ_3 -btz) ₆ (Cu{CNrBu}) 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 ₃ C ₆ H ₄ SO ₃ -4] ₂	C _i , rhombic compression	55	VT crystallography	55
[H ₃ NC ₆ H ₄ Cl-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
<i>trans</i> -[Cu(O ₂ CCH ₂ OCH ₃) ₂ (OH) ₂]	C _i , rhombic compression	64	VT crystallography	65
[Cu(HC{PPh ₂ O} ₃) ₂][ClO ₄] ₂	C _i , tetragonal compression	66	EXAFS VT crystallography and powder EPR	67 68
<i>cis</i> -[Cu(vanillinate)(OH) ₂]	C _{2v} , tetragonal compression	69	VT crystallography and TLS analysis	70
<i>trans</i> -[Cu(O ₂ NO) 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 ₂ O ^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 ₃ sar)][ClO ₄] ₄	S ₆ , trigonal distortion	79	VT powder EPR EPR of Cu-doped Zn analogue	79 79
<i>cis</i> -[Cu(ONO)(bipy) ₂]NO ₃ ^g	C ₁ , small rhombic elongation	80	VT crystallography	80
<i>cis</i> -[Cu(hat) ₂ (OH ₂) ₂][ClO ₄] ₂			VT powder EPR	82
[Cu(μ-dpp)(OH ₂) ₂] _n [BF ₄] _{2n} .2nH ₂ O ^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 ₂ O	C _i , tetragonal compression	88	VT powder and single crystal EPR	88

^aThe γ-phase of the same compounds exhibits a crystallographically ordered rhombically elongated octahedral Cu(II) centre.¹³ ^bThe solvated forms of these materials, [Cu(pyO)₆][NO₃]₂.2H₂O has a typical, static Jahn-Teller elongated geometry at 293 K.³³ ^cThe salts [Cu(dien)₂]Br₂⁴⁰ and [Cu(dien)₂]Cl[ClO₄]⁴¹ have a typical, static pseudo-Jahn-Teller elongated geometry at 293 K. ^dThe salt [Cu(terpy)₂][NO₃]₂ has a typical, static pseudo-Jahn-Teller elongated geometry at 298 K.⁴⁶ ^eThe salt [Cu(tach)₂][ClO₄]₂ has a typical, static Jahn-Teller elongated geometry at 293 K.⁵² ^fThe salts [Cu([9]aneN₃)₂][ClO₄]₂⁷⁶ and [Cu([9]aneN₃)₂]Cl₂⁷⁷ 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]aneN₃)₂][CF₃SO₄]₂.H₂O has a static Jahn-Teller elongation in the crystal.⁷⁷ ^gSeveral other fluxional complexes of type [Cu(X)(bipy)₂]Y, [Cu(X)(phen)₂]Y or [Cu(X)(bipyam)₂]Y (X⁻ = NO₂⁻ or MeCO₂⁻; Y⁻ = NO₃⁻, BF₄⁻, ClO₄⁻, PF₆⁻ etc.) have also been studied by VT crystallography.⁸¹ ^hThe isomorphous ClO₄⁻ salt of the same compound also probably contains fluxional Cu centres, although this was not studied.⁸⁴ ⁱThere are two independent molecules in the crystal structure of this compound. The other molecule has a static Jahn-Teller elongated structure.

1. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1971, **10**, 1264.
2. S. Takagi, M. D. Joesten and P. G. Lehner, *Acta Cryst., Sect. B*, 1976, **32**, 326.
3. S. Klein and D. Reinen, *J. Solid State Chem.*, 1978, **25**, 295.
4. M. D. Joesten, S. Takagi and P. G. Lenhert, *Inorg. Chem.*, 1977, **16**, 2681.
5. C. Friebel, *Z. Anorg. Allg. Chem.*, 1975, **417**, 197.
6. F. Villain, M. Verdagner and Y. Dromzee, *J. Phys. IV*, 1997, **7**, 659.
7. S. Takagi, M. D. Joesten and P. G. Lenhert, *J. Am. Chem. Soc.*, 1975, **97**, 444; S. Takagi, M. D. Joesten and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 1976, **32**, 1278.
8. R. Helmbold, D. Mullen, H. Ahsbahs, A. Klopsch, E. Hellner and G. Heger, *Z. Kristallogr.*, 1976, **143**, 220.
9. D. Mullen, G. Heger and D. Reinen, *Solid State Commun.*, 1975, **17**, 1249.
10. B. V. Harrowfield and J. R. Pilbrow, *J. Phys. C*, 1973, **6**, 755.
11. M. D. Joesten, S. Takagi and J. H. Venable jr., *Chem. Phys. Lett.*, 1975, **36**, 536.
12. D. Reinen, C. Friebel and K. P. Reetz, *J. Solid State Chem.*, 1972, **4**, 103.
13. S. Klein and D. Reinen, *J. Solid State Chem.*, 1980, **32**, 311.
14. K. Knox, *J. Chem. Phys.*, 1959, **30**, 991.
15. D. I. Khomskii and I. Kugel, *Solid State Commun.*, 1973, **13**, 763.
16. W. Kleeman and Y. Farge, *J. Phys.*, 1975, **36**, 1293; J. Ferre, M. Regis, Y. Farge and W. Kleemann, *Physica B+C*, 1977, **89**, 181; J. Ferre, M. Regis, Y. Farge and W. Kleemann, *J. Phys. C*, 1979, **12**, 2671.
17. R. Haegele and D. Babel, *Z. Anorg. Allg. Chem.*, 1974, **409**, 11; E. Herdtweck and D. Babel, *Z. Anorg. Allg. Chem.*, 1981, **474**, 113; D. Reinen and S. Krause, *Inorg. Chem.*, 1981, **20**, 2750.
18. M. E. Fleet, *Acta Cryst., Sect. B*, 1975, **31**, 183.
19. J. D. Grice, J. T. Szymanski and J. L. Jambor, *Canad. Mineral.*, 1996, **34**, 73.
20. H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, 1966, **20**, 659; G. M. Brown and R. Chidambaram, *Acta Crystallogr., Sect. B*, 1969, **25**, 676.
21. N. W. Alcock, M. Duggan, A. Murray, S. Tyagi, B. J. Hathaway and A. Hewat, *J. Chem. Soc., Dalton Trans.*, 1984, **7**.
22. B. J. Hathaway and A. W. Hewat, *J. Solid State Chem.*, 1984, **51**, 364.
23. M. A. Hitchman, W. Maaskant, J. van der Plas, C. J. Simmons and H. Strateimer, *J. Am. Chem. Soc.*, 1999, **121**, 1488.
24. B. N. Figgis, A. N. Soblelev, C. J. Simmons, M. A. Hitchman, H. Strateimer and M. J. Riley, *Acta Cryst., Sect. B*, 2000, **56**, 438.
25. M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150.
26. T. D. Waite and M. A. Hitchman, *Inorg. Chem.*, 1976, **15**, 2155.
27. C. J. O'Connor, E. Sinn and R. L. Carlin, *Inorg. Chem.*, 1977, **16**, 3314.
28. D. Taylor, *Aust. J. Chem.*, 1978, **31**, 713.
29. J. S. Wood, C. P. Keijzers, E. de Boer and A. Buttafava, *Inorg. Chem.*, 1980, **19**, 2213.
30. C. P. Keijzers, R. K. McMullan, J. S. Wood, G. van Kalkeren, R. Srinivasan and E. de Boer, *Inorg. Chem.*, 1982, **21**, 4275.
31. D. Reinen and S. Krause, *Solid State Commun.*, 1979, **29**, 691.
32. J. S. Wood, C. P. Keijzers and R. O. Day, *Acta Cryst., Sect. C*, 1984, **40**, 404.
33. I. Persson, P. Persson, M. Sandström and A.-S. Ullström, *J. Chem. Soc., Dalton Trans.*, 2002, 1256.
34. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858.
35. I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chim. Acta*, 1974, **11**, L17; I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1977, **26**, 1973.
36. M. Lutz, *Acta Cryst., Sect. C*, 2010, **66**, m330; S. Smeets, P. Parois, H.-B. Bürgi and M. Lutz, *Acta Cryst., Sect. B*, 2011, **67**, 53.
37. F. S. Stephens, *J. Chem. Soc. A*, 1969, 883.
38. A. Murphy, J. Mullane and B. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 129.
39. B. J. Hathaway, M. J. Bew and D. E. Billing, *J. Chem. Soc. A*, 1970, 1090.
40. F. S. Stephens, *J. Chem. Soc. A*, 1969, 2233.
41. M. Duggan, B. J. Hathaway and J. Mullane, *J. Chem. Soc., Dalton Trans.*, 1980, 690.
42. J.-V. Folgado, W. Henke, R. Allmann, H. Strateimer, D. Beltrán-Porter, T. Rojo and D. Reinen, *Inorg. Chem.*, 1990, **29**, 2035.
43. W. Henke and D. Reinen, *Z. Anorg. Allg. Chem.*, 1977, **436**, 187.
44. M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain and J. P. Declercq, *Acta Cryst., Sect. B*, 1982, **38**, 1323.
45. R. Docherty, F. Tuna, C. A. Kilner, E. J. L. McInnes and M. A. Halcrow, *Chem. Commun.*, 2012, **48**, 4055.
46. R. Allmann, W. Henke and D. Reinen, *Inorg. Chem.*, 1978, **17**, 378.
47. A. J. Amoroso, M. W. Burrows, S. J. Coles, R. Haigh, R. D. Farley, M. B. Hursthouse, M. Jones, K. M. A. Malik and D. M. Murphy, *Dalton Trans.*, 2008, 506.
48. N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 1998, **37**, 2221.
49. M. A. Leech, N. K. Solanki, M. A. Halcrow, J. A. K. Howard and S. Dahaoui, *Chem. Commun.*, 1999, 2245.
50. N. K. Solanki, M. A. Leech, E. J. L. McInnes, F. E. Mabbs, J. A. K. Howard, C. A. Kilner, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 1295.
51. G. S. Beddard, M. A. Halcrow, M. A. Hitchman, M. P. de Miranda, C. J. Simmons and H. Strateimer, *Dalton Trans.*, 2003, 1028.
52. N. K. Solanki, M. A. Leech, E. J. L. McInnes, J. P. Zhao, F. E. Mabbs, N. Feeder, J. A. K. Howard, J. E. Davies, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2001, 2083.
53. G. F. Kokoszka, J. Baranowski, C. Goldstein, J. Orsini, A. D. Mighell, V. I. Himes and A. R. Siedle, *J. Am. Chem. Soc.*, 1983, **105**, 5627.
54. J. H. Ammeter, H. B. Bürgi, E. Gamp, V. Meyer-Sandrin and W. P. Jensen, *Inorg. Chem.*, 1979, **18**, 733.
55. J. Bebenorf, H.-B. Bürgi, E. Gamp, M. A. Hitchman, A. Murphy, D. Reinen, M. J. Riley and H. Strateimer, *Inorg. Chem.*, 1996, **35**, 7419.
56. D. A. Tucker, P. S. White, K. L. Trojan, M. L. Kirk and W. E. Hatfield, *Inorg. Chem.*, 1991, **30**, 823.
57. M. Wei and R. D. Willett, *Inorg. Chem.*, 1995, **34**, 3780.
58. P. J. Ellis, H. C. Freeman, M. A. Hitchman, D. Reinen and B. Wagner, *Inorg. Chem.*, 1994, **33**, 1249.
59. H. Strateimer, B. Wagner, E. R. Krausz, R. Linder, H.-H. Schmidke, J. Pebler, W. E. Hatfield, L. ten Haar, D. Reinen and M. A. Hitchman, *Inorg. Chem.*, 1994, **33**, 2320.
60. B. Wagner, S. A. Warda, M. A. Hitchman and D. Reinen, *Inorg. Chem.*, 1996, **35**, 3967.
61. M. D. Joesten, M. S. Hussain and P. G. Lenhert, *Inorg. Chem.*, 1970, **9**, 151.
62. M. D. Joesten, R. C. Koch, T. W. Martin and J. H. Venable jr, *J. Am. Chem. Soc.*, 1971, **93**, 1138.
63. R. C. Koch, M. D. Joesten and J. H. Venable jr, *J. Chem. Phys.*, 1973, **59**, 6312.
64. C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc. A*, 1968, 2791.
65. K. Prout, A. Edwards, V. Mtetwa, J. Murray, J. F. Saunders and F. J. C. Rossotti, *Inorg. Chem.*, 1997, **36**, 2820; C. J. Simmons, H. Strateimer, M. A. Hitchman, D. Reinen, V. M. Masters and M. J. Riley, *Inorg. Chem.*, 2011, **50**, 4900.
66. S.-J. Shieh, C.-M. Che and S.-M. Peng, *Inorg. Chim. Acta*, 1992, **192**, 151.
67. V. M. Masters, M. J. Riley, M. A. Hitchman and C. Simmons, *Inorg. Chem.*, 2001, **40**, 4478.
68. C. J. Simmons, H. Strateimer, G. R. Hanson and M. A. Hitchman, *Inorg. Chem.*, 2005, **44**, 2753.
69. B. Kozlevčar, M. Humar, P. Strauch and I. Leban, *Z. Naturforsch., Teil B*, 2005, **60**, 1273.
70. B. Kozlevčar, A. Golobič and P. Strauch, *Polyhedron*, 2006, **25**, 2824.
71. M. F. Belicchi, G. V. Gasparri, C. Pelizzi and P. Tarasconi, *Transition Met. Chem.*, 1985, **10**, 295.
72. W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.
73. R. S. Glass, L. K. Steffen, D. D. Swanson, G. S. Wilson, R. de Gelder, R. A. G. de Graaf and J. Reedijk, *Inorg. Chim. Acta*, 1993, **207**, 241.
74. D. Reinen, A. Ozarowski, B. Jakob, J. Pebler, H. Strateimer, K. Wiegardt and I. Tolksdorf, *Inorg. Chem.*, 1987, **26**, 4010.
75. P. Chaudhuri, K. Oder, K. Wiegardt, J. Weiss, J. Reedijk, W. Hinrich, J. Wood, A. Ozarowski, H. Strateimer and D. Reinen, *Inorg. Chem.*, 1986, **25**, 2951.
76. A. D. Beveridge, A. J. Lavery, M. D. Walkinshaw and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1987, 373.
77. M. Kavana, D. R. Powell and J. N. Burstyn, *Inorg. Chim. Acta*, 2000, **297**, 351.
78. R. I. Sheldon, A. J. Ciritano, M. A. Beno, J. M. Williams and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3028.
79. P. V. Bernhardt, R. Bramley, L. M. Engelhardt, J. M. Harrowfield, D. C. R. Hockless, B. R. Korybut-

- Daszkiewicz, E. R. Krausz, T. Morgan, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1995, **34**, 3589.
80. C. J. Simmons, B. J. Hathaway, K. Amornjarusiri, B. D. Santarsiero and A. Clearfield, *J. Am. Chem. Soc.*, 1987, **109**, 1947.
81. C. J. Simmons, *New J. Chem.*, 1993, **17**, 77.
82. H. Grove, J. Sletten, M. Julve, F. Lloret, L. Lezama, J. Carranza, S. Parsons and P. Rillema, *J. Mol. Struct.*, 2002, **606**, 253.
83. H. Grove, J. Sletten, M. Julve, F. Lloret and L. Lezama, *Inorg. Chim. Acta*, 2000, **310**, 217.
84. L. W. Morgan, K. V. Goodwin, W. T. Pennington and J. D. Peterson, *Inorg. Chem.*, 1992, **31**, 1103.
85. A. Murphy, B. J. Hathaway and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1979, 1646.
86. C. A. Kilner, E. J. L. McInnes, M. A. Leech, G. S. Beddard, J. A. K. Howard, F. E. Mabbs, D. Collison, A. J. Bridgeman and M. A. Halcrow, *Dalton Trans.*, 2004, 236.
87. T. Astley, P. J. Ellis, H. C. Freeman, M. A. Hitchman, F. R. Keene, E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1995, 595.
88. T. Astley, H. Headlam, M. A. Hitchman, F. R. Keene, J. Pilbrow, H. Stratemeier, E. R. T. Tiekink and Y. C. Zhong, *J. Chem. Soc., Dalton Trans.*, 1995, 3809.

