

Diaquadifluorobis(nicotinamide)copper(II) Tetrahydrate: Hydrogen Bonding between Ligand Fluoride and Lattice Water†

John Emsley* and Naser M. Reza

Department of Chemistry, King's College, Strand, London WC2R 2LS

Helen M. Dawes and Michael B. Hursthouse

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Copper(II) fluoride, insoluble in water, dissolves easily in an aqueous solution of nicotinamide from which grow blue crystals of the compound $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (na = nicotinamide). The X-ray crystal structure of this complex shows not only rare copper-fluoride bonds but equally rare ligand fluoride-lattice water hydrogen bonds. There are three such kinds of bond with $R(\text{F} \cdots \text{O}) = 2.683, 2.727, \text{ and } 2.853 \text{ \AA}$. Other properties of this compound are also reported.

Hydrated fluoride ions, $[\text{F} \cdot n\text{H}_2\text{O}]^-$, undoubtedly exist in solution and a lot of speculation has been generated about their structure and hydrogen bonding.¹ To date no simple hydrated fluoride has been found in a crystal lattice so that theoretical computations about the length and strength of the hydrogen bonding remain unconfirmed.² Indeed relatively few metal fluoride hydrates have been examined by X-ray crystallography,³ but recently a few complexes with fluoride ligands have been reported in which $\text{F}^- \cdots \text{H}-\text{OH}$ bonds are also present: $\text{Hg}_2\text{AlF}_5 \cdot 2\text{H}_2\text{O}$,⁴ $[\text{W}(\text{PMe}_3)_4\text{H}_2(\text{H}_2\text{O})\text{F}]\text{F}$,⁵ and $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$ (Him = imidazole).⁶ In the tungsten complex there are intramolecular hydrogen bonds between the ligand H_2O and $\text{W}-\text{F}$ as well as very short hydrogen bonds between the ligand water and lattice fluoride, with a very short $R(\text{F} \cdots \text{O})$ of 2.40 Å.⁵ In the copper complex there are similar types of hydrogen bonding but longer values (2.695, 2.717 Å),⁶ although each fluoride forms four hydrogen bonds, two to water and two to the NH of the imidazole ligands.

Recently a fluoride-inhibited enzyme, cytochrome c peroxidase, has been examined by X-ray crystallography and shown to have a fluoride as ligand to the iron of the haem site.⁷ This fluoride then attracts NH bonds on neighbouring histidine and arginine groups and *via* these hydrogen bonds it disables the enzyme. Hydrogen bonding to nearby water molecules is rejected in favour of $\text{F} \cdots \text{H}-\text{N}$ bonds.

Copper ions are of biological significance in cofactors, metalloenzymes, and metalloproteins.⁸ In searching for a system with hydrated fluoride ions we are investigating metal fluorides and solutions in which they are soluble, and from which hydrates might be crystallised. One system of copper fluoride and nicotinamide (na) produced excellent specimens, and this combination is relevant to these natural biological copper-containing substances because na has been shown to be metabolically linked to copper. Nicotinamide is one form of niacin and a deficiency of this vitamin leads to loss of copper from the body.⁹ Moreover one copper-nicotinamide complex is already known $[\text{Cu}(\text{na})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2] \cdot 2\text{H}_2\text{O}$ in which the tetrafluoroborate ions occupy the more distant of the pseudo-octahedral ligand sites around the copper.¹⁰

Experimental

Synthesis of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$.—Copper(II) fluoride (0.5 g, 5 mmol) was added to a solution of na (1.2 g, 10

mmol) in water (50 cm³) and dissolved on stirring and warming to give a beautiful clear blue solution after 2 h. The volume of the solution was reduced by half on a rotary evaporator, and on standing overnight large blue crystals formed that are stable in air (Found: C, 31.85; H, 5.15; N, 12.4. Calc. for $\text{C}_{12}\text{H}_{24}\text{CuF}_2\text{N}_4\text{O}_8$: C, 31.75; H, 5.35, N, 12.35%), m.p. 235 °C (decomp.). On standing, or more rapidly on heating, the crystals slowly turn pale blue due to dehydration. A sample of the complex treated with acid on a glass slide did not result in etching.

The solubility of CuF_2 in a 0.200 mol dm⁻³ solution of na is 13.33 g dm⁻³ which is 0.131 mol dm⁻³. The complex is very soluble in glacial acetic acid, moderately soluble in formamide, but insoluble in diglyme (2,5,8-trioxanonane), dimethyl sulphoxide, and dimethylformamide.

Infrared spectra (5 000—180 cm⁻¹) were recorded on a model 983G Perkin-Elmer i.r. spectrometer using Nujol and hexachlorobutadiene mulls. The significant peaks and likely assignments are 3 570(sh), 3 402vs, br, 3 203vs (both hydrogen bonded OH and NH modes), 1 692vs (na), 1 631 [$\delta(\text{H}_2\text{O})$], 1 604s (na), 1 573m (na), 1 433m (na), 1 194m (na), 1 154w (na), 1 131m (na), 1 059m, 1 034w (na), 965w (na), 842m (na), 763 [$\omega(\text{H}_2\text{O})$], 721s (na), 697s (na), 657w [$\nu(\text{CuF})$], 550m, br (H_2O), 500(sh) [$\nu(\text{CuN})$], 443m [$\delta(\text{CuF})$], 285w [$\delta(\text{CuN})$], and 216m cm⁻¹ (na) (na = nicotinamide mode). Deuteriation of the complex by twice recrystallising it from D₂O shifted the broad collection of hydrogen-bonding modes centred at *ca.* 3 400 and 550 cm⁻¹ to 2 500 and 450 cm⁻¹ respectively.

The u.v. spectrum of an aqueous solution was recorded on a model SP8-100 UV/VIS Perkin-Elmer spectrometer and showed a band maximum at 763 nm ($\epsilon_{\text{max.}} = 48 \text{ m}^2 \text{ mol}^{-1}$).

X-Ray Structure Determination.—Crystal data were collected on an Enraf-Nonius CAD-4 diffractometer using a ω -2 θ scan procedure.¹¹

Crystal data. $\text{C}_{12}\text{H}_{24}\text{CuF}_2\text{N}_4\text{O}_8$, $M = 453.89$, triclinic, $a = 8.895(1)$, $b = 8.008(1)$, $c = 7.222(1) \text{ \AA}$, $\alpha = 110.57(1)$, $\beta = 103.11(1)$, $\gamma = 90.36(1)^\circ$, space group $P\bar{1}$, $U = 467.003 \text{ \AA}^3$, $Z = 1$, $D_c = 1.614 \text{ g cm}^{-3}$, $F(000) = 235$, $\mu(\text{Mo}-K_\alpha) = 11.70 \text{ cm}^{-1}$, $\lambda = 0.71069 \text{ \AA}$, $T = 20 \text{ }^\circ\text{C}$, crystal dimensions = $0.46 \times 0.28 \times 0.24 \text{ mm}$.

Data collection, solution, and refinement. The intensities of 2 251 reflections ($\theta_{\text{max.}} = 28^\circ$) were measured of which 2 181 satisfied the criterion $I > 1.5\sigma(I)$ and were used in the refinement. The structure was solved *via* the heavy-atom method, the Cu atom lying on a centre of inversion at (0,0,0). Refinement proceeded by standard full-matrix least squares.¹² All hydrogens were located and refined freely with individual isotropic thermal parameters; all other atoms were assigned

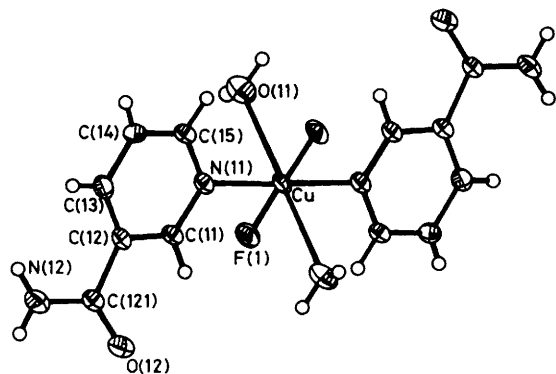
† Supplementary data available (No. SUP 56367, 5 pp.): thermal parameters, H-atom co-ordinates, bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$

Atom	x	y	z
Cu(1)	0	0	0
F(1)	-90(1)	1 151(1)	-1 930(1)
O(11)	569(2)	-2 919(2)	-2 566(2)
N(11)	2 305(1)	623(2)	996(2)
C(11)	2 936(2)	2 250(2)	1 286(2)
C(12)	4 493(2)	2 804(2)	2 177(2)
C(121)	5 042(2)	4 698(2)	2 540(2)
O(12)	4 113(1)	5 826(2)	2 548(2)
N(12)	6 562(2)	5 086(2)	2 905(3)
C(13)	5 433(2)	1 615(2)	2 774(2)
C(14)	4 789(2)	-71(2)	2 448(2)
C(15)	3 231(2)	-517(2)	1 566(2)
O(1)	1 103(2)	6 104(2)	3 143(3)
O(2)	1 823(2)	1 343(2)	5 750(2)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$

F(1)-Cu(1)	1.911(3)	O(11)-Cu(1)	2.560(4)
N(11)-Cu(1)	2.009(3)	C(11)-N(11)	1.342(3)
C(15)-N(11)	1.342(3)	C(12)-C(11)	1.385(3)
C(121)-C(12)	1.504(4)	C(13)-C(12)	1.388(3)
O(12)-C(121)	1.227(3)	N(12)-C(121)	1.331(3)
C(14)-C(13)	1.382(3)	C(15)-C(14)	1.374(3)
N(11)-Cu(1)-F(1)	90.7(0.5)	O(11)-Cu(1)-F(1)	90.4(0.5)
O(11)-Cu(1)-N(11)	87.1(0.5)	C(11)-N(11)-Cu(1)	120.7(2)
C(15)-N(11)-Cu(1)	120.6(2)	C(15)-N(11)-C(11)	118.4(2)
C(12)-C(11)-N(11)	122.6(2)	C(121)-C(12)-C(12)	117.6(2)
C(13)-C(12)-C(11)	118.3(2)	C(13)-C(12)-C(12)	124.0(2)
O(12)-C(121)-C(12)	120.5(2)	N(12)-C(121)-C(121)	117.0(2)
N(12)-C(121)-O(12)	122.5(2)	C(14)-C(13)-C(12)	119.1(2)
C(15)-C(14)-C(13)	119.2(2)	C(14)-C(15)-N(11)	122.4(2)

**Figure 1.** Structure and atom labelling of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2]$

anisotropic thermal parameters. The final R value was 0.0259 and $R' = (\sum w\Delta F^2 / \sum wF_o^2)^{1/2} = 0.0352$. The weighting scheme used was $w = 1 / (\sum^2 F_o + gF_o^2)$, where $g = 0.00004$.

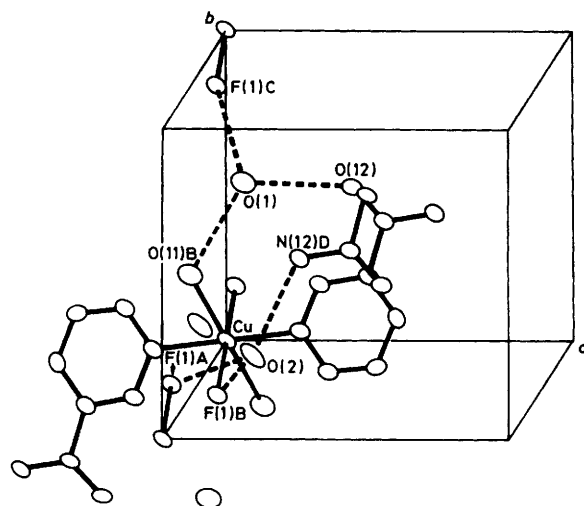
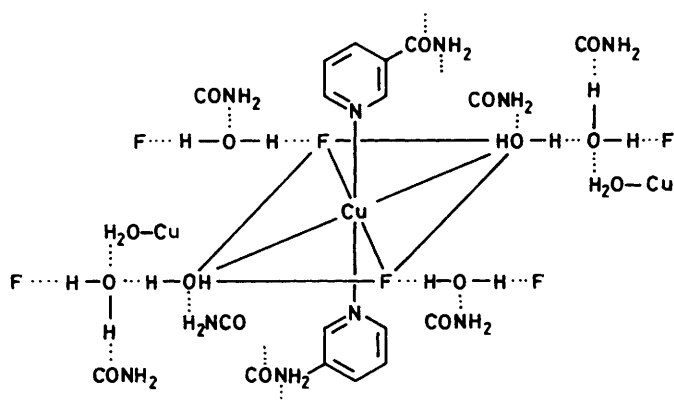
Table 1 lists the atomic co-ordinates, Table 2 the bond lengths and angles of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2]$ whose structure is shown in Figure 1. A section of the structure viewed perpendicular to the ab face of the unit cell is shown in Figure 2 and the hydrogen-bond data for the lattice ligand (011) and waters, (01) and (02), are given in Table 3 and shown diagrammatically in Figure 3.

Discussion

Copper(II) fluoride dissolves in water to the extent of only 0.75 g dm^{-3} .¹³ However it is soluble in an aqueous solution of

Table 3. Hydrogen bonds of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$

	Distance/ \AA		Symmetry operation
O(1) ... O(12)	2.805		x, y, z
O(1) ... F(1)	2.727	C	$-x, 1-y, -z$
O(1) ... O(11)	2.795	B	$-x, -y, -z$
O(2) ... F(1)	2.683	A	$x, y, 1+z$
O(2) ... F(1)	2.853	B	$-x, -y, -z$
O(2) ... N(12)	2.923	D	$1-x, 1-y, 1-z$
O(11) ... N(12)	3.103		$1-x, -y, -z$
O(1) ... O(11)	3.067		$x, 1+y, 1+z$

**Figure 2.** Unit cell of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ showing the hydrogen-bonding network to lattice waters**Figure 3.** Hydrogen-bond network of $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$

nicotinamide, to the extent of 13.33 g dm^{-3} ($0.131 \text{ mol dm}^{-3}$) in a 0.2 mol dm^{-3} solution at 20°C . Evaporation of such solutions yields blue crystals of composition $\text{Cu}(\text{na})_2\text{F}_2 \cdot 6\text{H}_2\text{O}$ and these have been fully analysed by X -ray crystallography. Somewhat disappointingly they do not harbour hydrated fluoride ions, nor do they contain examples of a Cu-F ligand hydrogen bonding to the NH of nicotinamide. Nevertheless they do possess another rare type of interaction: ligand fluoride to lattice water and are unique in having Cu-F ... HOH hydrogen bonds.

The Copper Complex.—Figure 1 shows the arrangement of ligands around the copper in $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2]$. This atom

Table 4. Classification of F...H-OH hydrogen bonds

	$R(\text{F} \cdots \text{O})/\text{\AA}$	Ref.		$R(\text{F} \cdots \text{O})/\text{\AA}$	Ref.
Ligand H_2O -lattice F^-			Lattice H_2O -ligand F^-		
[W(PMe ₃) ₄ H ₂ (H ₂ O)F]F	2.40	5	Rb[VF ₄]-2H ₂ O	2.56	31
[NH ₄] ₂ [Cr(H ₂ O) ₆]F ₅	2.53, 2.57	29	Rb ₂ [AlF ₅]-H ₂ O	2.79	c
[Cr(H ₂ O) ₆]F ₃ ·3H ₂ O	2.61	30	Sr[TiF ₆]-2H ₂ O	2.75, 2.77	d
[Cu(Him) ₄ (H ₂ O) ₂]F ₂	2.695, 2.717	6	[Cu(na) ₂ F ₂ (H ₂ O) ₂]-4H ₂ O	2.683, 2.727, 2.853	This work
Average = 2.59			Average = 2.73		
Ligand H_2O -ligand F^-			Lattice H_2O -lattice F^-		
[Hg ₂ (H ₂ O) ₂][AlF ₃]	2.584	4	NMe ₄ F·4H ₂ O	2.63	23
[CuF ₂ (H ₂ O) ₂]	2.717	14	[Cu(H ₂ O)(bipyam)F]F·3H ₂ O	2.659	e
[Zn(H ₂ O) ₄][InF ₃]-3H ₂ O	2.62-2.73 (12, average = 2.66)	26	Average = 2.65		
Cs[MnF ₄ (H ₂ O) ₂]	2.661, 2.630	a			
[Cd(H ₂ O) ₄][GaF ₃]-3H ₂ O	2.63-2.86 (13, average = 2.73)	26			
[Co(H ₂ O) ₆][SiF ₆]	2.711, 2.785	b			
Average = 2.70					

^a P. Bukovec and V. Kaučič, *J. Chem. Soc., Dalton Trans.*, 1977, 945. ^b H. Luntton, and P.-Y. Siew, *Can. J. Chem.*, 1973, **51**, 227. ^c J. L. Fourquet, F. Plet, and R. De Pape, *Rev. Chim. Min.*, 1981, **18**, 19. ^d B. V. Bukvetsky, R. L. Davidovich, and V. I. Simonov, *Coord. Chem.*, 1975, **1**, 1558. ^e R. A. Jacobson and W. P. Jensen, *Inorg. Chim. Acta*, 1981, **52**, 205; bipyam = bis(2-pyridyl)amine.

sits at a centre of inversion of a pseudo-octahedral array explicable by Jahn-Teller effects. The Cu-N and Cu-OH₂ bonds are as expected.

Fluoride is not often encountered as a ligand for copper and uncomplicated Cu-F bonds are very rare, so there is little with which to compare the 1.911(3) Å bond length. The Cu-F bond length in CuF₂·2H₂O is 1.906(1) Å,¹⁴ 1.93(3) Å in crystalline CuF₂,¹⁵ 1.72(-) Å, in the vapour phase,¹⁶ 1.91(3) Å in Na₂CuF₄,¹⁷ 1.89(1) and 1.96(1) Å in KCuF₃,¹⁸ and 1.95(3) and 2.08(3) Å in K₂CuF₄.¹⁹ A fluorine-bridged complex, [Cu₂F₂(Hdmpz)₂(Hmpz)₄][BF₄]₂ (Hdmpz = 3,5-dimethylpyrazole, Hmpz = 5-methylpyrazole), has $R(\text{Cu}-\text{F})$ 1.904(2) and 2.258(2) Å.²⁰ Finally the complex [Cu(na)₂(H₂O)₂(BF₄)₂]-2H₂O has $R(\text{Cu}-\text{F})$ = 2.48(1) Å involving the tetrafluoroborate ligands which occupy the pseudo-octahedral positions.¹⁰

The Hydrogen-bonding Framework.—The neutral copper complexes are held together by lattice waters which form a network of hydrogen bonds as shown in Figure 3. These O-H...F, O-H...N, and O-H...O bonds are mostly short but there is also a weak hydrogen bond between a ligand water and the amide nitrogen on an adjacent complex.

Early investigation of the fluoride hydrates KF·2H₂O,²¹ KF·4H₂O,²² NMe₄F·4H₂O,²³ and NBu₄F·H₂O²⁴ found $R(\text{F} \cdots \text{O})$ in the range 2.61-2.79 Å but no discrete [F·*n*H₂O]⁻ units. An analysis of metal fluoride F...H-O bonds in 1978 by Simonov and Bukvetsky³ showed $R(\text{F} \cdots \text{O})$ = 2.56-2.86 Å with an average of 2.68 Å for the 40 such bonds they could find in the literature, although many of these were variants within the same crystal, e.g. ZnF₂·4H₂O has six,²⁵ ZnInF₃·7H₂O twelve,²⁶ and CdGaF₄·7H₂O thirteen²⁶ different $R(\text{F} \cdots \text{O})$ distances. The mean OHF angle was 170°.

The shortest F...H-O bonds are not found in fluoride hydrates but in KH₂PO₃·HF (2.383 Å)²⁷ and KF·(CH₂CO₂H)₂ (2.441 Å).²⁸ The examples with the closest fluoride-to-water hydrogen bonds are found in complexes such as [NH₄]₂[Cr(H₂O)₆]F₅, 2.53-2.57,²⁹ [Cr(H₂O)₆]F₃·3H₂O, 2.61,³⁰ Rb[VF₄]-2H₂O, 2.56,³¹ and ZnF₂·4H₂O, 2.57 Å.²⁵ An attempt at classifying F...HOH hydrogen bonds has been made in Table 4. In theory we expect the order to be ligand H₂O-lattice F⁻ < ligand H₂O-ligand F⁻ < lattice H₂O-lattice F⁻ < lattice H₂O-ligand F⁻, since complexing should reduce the ability of F⁻ to act as a hydrogen-bond acceptor and increase the polarity of the OH bond of water thereby making it a better hydrogen-bond donor. The average values in Table 4 are in

accord with these generalisations and we can predict that the $R(\text{F} \cdots \text{O})$ bond for F⁻...HOH as a discrete entity in a crystal will be ca. 2.65 Å. So far the nearest we come to this is in NMe₄F·4H₂O, where each fluoride is hydrogen bonded to four water molecules in a flattened tetrahedral arrangement with $R(\text{F} \cdots \text{O})$ = 2.63 Å. These water molecules are also linked to other waters in a complex hydrogen-bonded network.

References

- Gmelin Handbook of Inorganic Chemistry, 8th edn., Fluorine Supplement vol. 3, System number 5, Springer, Berlin, 1982, p. 299 *et seq.*
- J. Emsley, R. J. Parker, and R. E. Overill, *J. Chem. Soc., Faraday Trans. 2*, 1983, 1347 and refs. therein.
- V. I. Simonov and B. V. Bukvetsky, *Acta Crystallogr., Sect. B*, 1978, **34**, 355.
- J. L. Fourquet, F. Plet, and R. De Pape, *Acta Crystallogr., Sect. B*, 1981, **37**, 2136.
- M. L. H. Green, G. Parkin, C. Mingqin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 1400.
- W. Vreugdenhill, P. J. M. W. L. Birker, R. W. M. ten Hoedt, G. C. Verschoor, and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1984, 429.
- S. L. Edwards, T. L. Poulos, and J. Krant, *J. Biol. Chem.*, 1984, **259**, 12984.
- R. J. Kutsy, 'Handbook of Vitamins, Minerals and Hormones,' 2nd edn., Van Nostrand-Reinhold, New York, 1981, ch. 9, p. 101.
- K. A. R. U. Krishnamachari, *Am. J. Clin. Nutr.*, 1974, **27**, 108.
- B. L. Kindberg, E. H. Griffith, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1977, 461.
- M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
- G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
- Lange's Handbook of Chemistry, 12th edn., ed. J. A. Dean, McGraw-Hill, New York, 1974, sect. 4.48.
- S. C. Abrahams and E. Prince, *J. Chem. Phys.*, 1962, **36**, 50; S. C. Abrahams, *ibid.*, p. 56; E. Prince, *ibid.*, 1972, **56**, 4352.
- C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, 1957, **79**, 1049.
- L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, 1963, **63**, 111.
- K. Knox, *J. Chem. Phys.*, 1959, **30**, 991.
- A. Okazaki and Y. Suemune, *J. Phys. Soc. Jpn.*, 1961, **16**, 176.
- D. Reinen and C. Freebel, *Struct. Bonding (Berlin)*, 1979, **37**, 1.
- R. W. M. ten Hoedt, J. Reedijk, and G. C. Verschoor, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 400.
- T. H. Anderson and E. C. Lingafelter, *Acta Crystallogr.*, 1951, **4**, 181.
- G. Buerkens and G. A. Jeffrey, *J. Chem. Phys.*, 1964, **40**, 917.
- W. J. McLean and G. A. Jeffrey, *J. Chem. Phys.*, 1967, **41**, 414.

- 24 R. K. McMullan, M. Bonhomico, and G. A. Jeffrey, *J. Chem. Phys.*, 1963, **39**, 3295.
- 25 B. V. Bukvetsky, S. A. Polishchuk, and V. I. Simonov, *Kristallografiya*, 1973, **18**, 956.
- 26 B. V. Bukvetsky, S. A. Polishchuk, and V. I. Siminov, *Coord. Chem.*, 1977, **3**, 926.
- 27 H. Attenburg and D. Mootz, *Acta Crystallogr., Sect. B*, 1971, **27**, 1982.
- 28 J. Emsley, D. J. Jones, and R. S. Osborn, *J. Chem. Soc., Dalton Trans.*, 1982, 809.
- 29 W. Massa, *Z. Anorg. Allg. Chem.*, 1977, **436**, 29.
- 30 M. Epple and W. Massa, *Z. Anorg. Allg. Chem.*, 1977, **444**, 47.
- 31 B. V. Bukvetsky, L. A. Muradyan, R. L. Davidovich, and V. I. Simonov, *Sov. J. Coord. Chem. (Engl. Transl.)*, 1976, **2**, 869.

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