Structure of μ-Fluoro-bis[bis(2,2′-bipyridyl)fluoronickel(II)] Fluoride–Ethanol (1/2) Trihydrate, revealing Several Unique Features including Strong Hydrogen Bonds between Fluoride Ions and Ethanol Molecules[†]

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The crystal structure of the compound $[(bipy)_2FNi{-}F{-}NiF(bipy)_2]^+[F(EtOH)_2(H_2O)_2]^-\cdot H_2O$ (bipy = 2,2′-bipyridine) has been determined, providing examples of three different and rare fluoride environments: ligand, bridging, and ethanol-solvated ion. The ligand fluorides are linked by hydrogen bonding to the same water molecule and the torsion angle between them is 65°. The lattice fluoride ion is hydrogen bonded strongly to two ethanol molecules with $R(F \cdots O) = 2.579$ Å and to two water molecules with $R(F \cdots O) = 2.709$ Å.

Recently Higgins and Levason[1] have reported that nickel(II) fluoride hydrate, $NiF_2\cdot 4H_2O$, reacts with diamines and diimines to form complexes of the type $[NiL_3]F_2$, where L is a variety of common ligands, including 2,2′-bipyridine (bipy). Further reaction of these complexes with $NiF_2\cdot 4H_2O$ produces a second type of complex with the general formula NiL_2F_2 which was deduced to be the double-bridged species, $[L_2Ni(\mu\text{-}F)_2NiL_2]F_2$. These complexes were all obtained as anhydrous materials by the use of methanol as the solvent and 2,2-dimethoxypropane as a dehydrating agent. The products with bipy were pink $[Ni(bipy)_3]F_2$ and green $[Ni_2(bipy)_4F_2]F_2$.

Our interest in fluoride complexes arises from the possibility of involving the fluoride ligand in strong hydrogen bonding. This, we believe, is the key to the common practice of deactivating enzymes by the addition of fluoride. One such fluoride-poisoned enzyme, cytochrome c oxidase, has been analysed by *X*-ray diffraction and shown to have the iron at the active site complexed by fluoride.[2] This ligand then deforms the enzyme by hydrogen bonding to nearby groups.

In practice we have found it difficult to predict the structure of complexes that form from solutions of metal fluorides and ligands. Four kinds of hydrogen-bonded compound may be found depending on whether both fluoride and water act as ligands, or neither. Examples of ligand fluoride–lattice water,[3] ligand water–lattice fluoride,[4] lattice fluoride–lattice water,[5] and ligand fluoride–ligand water[6,7] interactions have all been uncovered, generally in copper and zinc complexes. These metals are found in many enzymes.

Our attention has now been drawn to nickel complexes. These are possible models for the active centres of the nickel enzymes that have recently been discovered, *e.g.* jack bean urease.[8] This contains 12 Ni atoms per enzyme molecule and was the first nickel enzyme to be identified. Several others have been reported since.[9]

Experimental

Synthesis of μ-Fluoro-bis[bis(2,2′-bipyridyl)fluoronickel(II)] Fluoride–Ethanol (1/2) Trihydrate.—A suspension of powdered $NiF_2\cdot 4H_2O$ (0.85 g, 5 mmol) in methanol (50 cm^3) was refluxed with 2,2′-bipyridine (1.82 g, 11 mmol). After 10 h a blue-purple solution was obtained and almost all the nickel salt had dissolved. The solution was cooled, filtered, and the volume reduced to about one-third on a rotary evaporator. It was then allowed to stand, and after 2 d a mixture of pink and green crystals was obtained. These dissolved in ethanol and from this solution grew well formed green crystals of μ-fluoro-bis[bis(2,2′-bipyridyl)fluoronickel(II)] fluoride–ethanol (1/2) trihydrate, m.p. 265 °C (decomp.) (Found: C, 54.60; H, 5.15; N, 11.40. $C_{44}H_{50}F_4N_8Ni_2O_5$ requires C, 54.75; H, 5.20; N, 11.60%).

The i.r. spectrum, run on a Perkin-Elmer 983G spectrometer, as a KBr disc, showed absorbances at 3 375vs br, 2 328m br, 1 672m br, 1 598vs, 1 564m, 1 489m, 1 471s, 1 442vs, 1 312m, 1 247w, 1 170w, 1 152m, 1 101w, 1 058m, 1 022s, 906m, 895m br, 813m, 771vs, 737s, 653m, 634m, 600—500m br, 410s, 380m, 360m, and 281w cm^{-1}.

The u.v. spectrum of an ethanolic solution showed an absorbance at 550 nm, $\varepsilon_{max.} = 15.79$ dm^3 mol^{-1} cm^{-1}. The conductivity of a 1.71×10^{-3} mol dm^{-3} solution in ethanol was 83 μS cm^{-1}.

X-Ray Structure Determination.—*Crystal data.* $C_{44}H_{50}F_4N_8Ni_2O_5$, $M = 964.34$, monoclinic, space group $C2/c$, $a = 12.874(1)$, $b = 18.727(4)$, $c = 18.849(2)$ Å, $\beta = 105.10(1)°$, $U = 4\,387(1)$ Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $F(000) = 2\,008$, $\mu(\text{Mo-}K_\alpha) = 9.3$ cm^{-1}, crystal size $0.65 \times 0.38 \times 0.25$ mm.

Data collection. Unit-cell dimensions were determined and intensity data collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω—2θ scan procedure.[10] A total of 4 194 unique reflections were collected ($3 < 2\theta < 50°$). The segment of reciprocal space scanned was: (h) 0 to 15, (k) 0 to 22, (l) −22 to 22. The reflection intensities were corrected for absorption using the azimuthal-scan method;[11] maximum transmission factor 1.00, minimum 0.94.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX 86),[12] and refined by full-matrix least squares (SHELX 76).[13] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the bipy ligands placed in calculated positions (C–H 0.96 Å; $U = 0.10$ Å^2). Hydrogen atoms of the ethanol and water molecules were not included in the model. The final residuals R and R' were 0.046 and 0.048 respectively for the 286 variables and 2 959 data for which $F_o > 3\sigma(F_o)$. The

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates (× 10^4) for $[(bipy)_2FNi–F–NiF(bipy)_2]F·2EtOH·3H_2O$

Atom	*x*	*y*	*z*
Ni	424.1(4)	1 316.7(2)	1 564.0(3)
F(1)	0	1 232(2)	2 500
F(2)	1 276(2)	413(1)	1 810(1)
F(3)	5 000	630(4)	2 500
O(1)	4 311(5)	1 125(5)	1 184(4)
O(2)	0	−435(2)	2 500
O(3)	3 212(3)	−125(2)	2 519(2)
N(1)	−920(3)	773(2)	970(2)
N(2)	660(3)	1 332(2)	502(2)
N(3)	1 710(3)	1 990(2)	2 019(2)
N(4)	−311(3)	2 334(2)	1 401(2)
C(1)	−1 690(3)	501(2)	1 256(3)
C(2)	−2 552(4)	115(2)	830(3)
C(3)	−2 599(4)	5(3)	104(3)
C(4)	−1 803(4)	274(2)	−194(3)
C(5)	−977(3)	664(2)	252(2)
C(6)	−107(3)	994(2)	−10(2)
C(7)	−69(4)	955(2)	−740(2)
C(8)	768(4)	1 275(3)	−941(3)
C(9)	1 539(4)	1 626(3)	−418(3)
C(10)	1 470(4)	1 635(2)	300(3)
C(11)	2 720(3)	1 778(2)	2 317(2)
C(12)	3 540(4)	2 257(3)	2 567(3)
C(13)	3 334(4)	2 983(3)	2 499(3)
C(14)	2 301(4)	3 208(2)	2 202(2)
C(15)	1 496(3)	2 699(2)	1 961(2)
C(16)	353(4)	2 885(2)	1 647(2)
C(17)	−12(5)	3 582(2)	1 618(3)
C(18)	−1 117(5)	3 707(3)	1 336(3)
C(19)	−1 793(4)	3 148(3)	1 078(3)
C(20)	−1 363(4)	2 458(3)	1 124(3)
C(21)	5 093(11)	1 619(7)	347(6)
C(22)	5 123(7)	1 063(7)	855(5)

Table 2. Selected bond lengths (Å) and angles (°) for $[(bipy)_2FNi–F–NiF(bipy)_2]F·2EtOH·3H_2O$

F(1)–Ni	1.985(3)	F(2)–Ni	2.005(4)
N(1)–Ni	2.067(5)	N(2)–Ni	2.101(5)
N(3)–Ni	2.080(5)	N(4)–Ni	2.114(5)
C(22)–O(1)	1.352(11)	C(22)–C(21)	2.407(16)
F(2)–Ni–F(1)	89.3(2)	N(1)–Ni–F(1)	93.3(2)
N(1)–Ni–F(2)	92.3(2)	N(2)–Ni–F(1)	171.6(1)
N(2)–Ni–F(2)	91.5(2)	N(2)–Ni–N(1)	78.4(2)
N(3)–Ni–F(1)	93.2(2)	N(3)–Ni–F(2)	95.0(2)
N(3)–Ni–N(1)	170.3(1)	N(3)–Ni–N(2)	95.0(2)
N(4)–Ni–F(1)	89.1(2)	N(4)–Ni–F(2)	172.7(1)
N(4)–Ni–N(1)	94.9(2)	N(4)–Ni–N(2)	91.1(2)
N(4)–Ni–N(3)	78.0(2)	Ni–F(1)–Ni(′)	170.8(2)
C(1)–N(1)–Ni	124.7(4)	C(5)–N(1)–Ni	115.9(4)
C(10)–N(2)–Ni	126.7(4)	C(6)–N(2)–Ni	114.6(4)
C(11)–N(3)–Ni	125.3(4)	C(15)–N(3)–Ni	116.0(4)
C(20)–N(4)–Ni	125.6(4)	C(16)–N(4)–Ni	115.0(4)
C(21)–C(22)–O(1)	111.2(12)		

The mean bond lengths of the bipyridyl rings are: C–C 1.381(8) and C–N 1.343(6) Å, and the interconnecting C(5)–C(6) bonds are 1.475(7) Å. Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (′) −*x*, *y*, 0.5 − *z*.

Table 3. Hydrogen bonds of $[(bipy)_2FNi–F–NiF(bipy)_2]F·2EtOH·3H_2O$; bond lengths in (Å) (see Figure 1)

F(2) ··· O(2)	2.833	F(2′) ··· O(2)	2.833
F(2) ··· O(3)	2.697		
F(3) ··· O(1)	2.579	F(3) ··· O(1″)	2.579
F(3) ··· O(3)	2.709	F(3) ··· O(3″)	2.709

Symmetry operations (′): −*x*, *y*, 0.5 − *z* and (″): 1.0 − *x*, *y*, 0.5 − *z*.

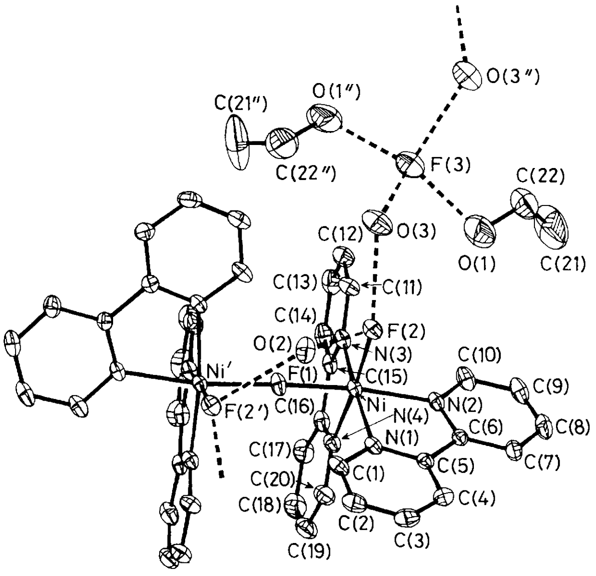

Figure 1. Structure and atom labelling of $[(bipy)_2FNi–F–NiF(bipy)_2]F·2EtOH·3H_2O$

function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, $w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 14 and 15 respectively. All computations were made on a DEC VAX-11/750 computer. Table 1 lists the atomic co-ordinates, Table 2 selected bond lengths and angles, and Table 3 the hydrogen bonds. A small portion of the lattice is shown in Figure 1. This shows the nickel complex bound by hydrogen bonds to an $[F(EtOH)_2(H_2O)_2]^-$ unit. The unit-cell packing diagram, Figure 2, displays the network of O ··· F hydrogen bonds that exist throughout the whole lattice.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Discussion

In recent papers we have reported on a variety of copper fluoride complexes with strong hydrogen bonds between fluoride and water.[3–5] Complexes of metals with fluoride ligands are relatively little studied. However, recently a series of nickel fluoride complexes has been reported.[1] The *X*-ray structure of the solvated form of one of these complexes is the subject of this paper.

The compound μ-fluoro-bis[bis(2,2′-bipyridyl)fluoronickel-(II)] fluoride–ethanol (1/2) trihydrate is reported here for the first time. It has three uncommon structural features: first, it is an example of a nickel complex with a fluoride ligand; second, it contains a fluoride bridge; and third, the lattice contains the fluoride counter ion, solvated by two water and two ethanol molecules. The crystal lattice contains four different examples of F ··· H–O hydrogen bonding, one of which can be classed as short.

Nickel complexes incorporating a fluoride ligand are rarely encountered; indeed a major review of nickel mentions none.[16] Another review of fluoro-bridged co-ordination compounds of first-row transition metals mentions only three.[17] However,

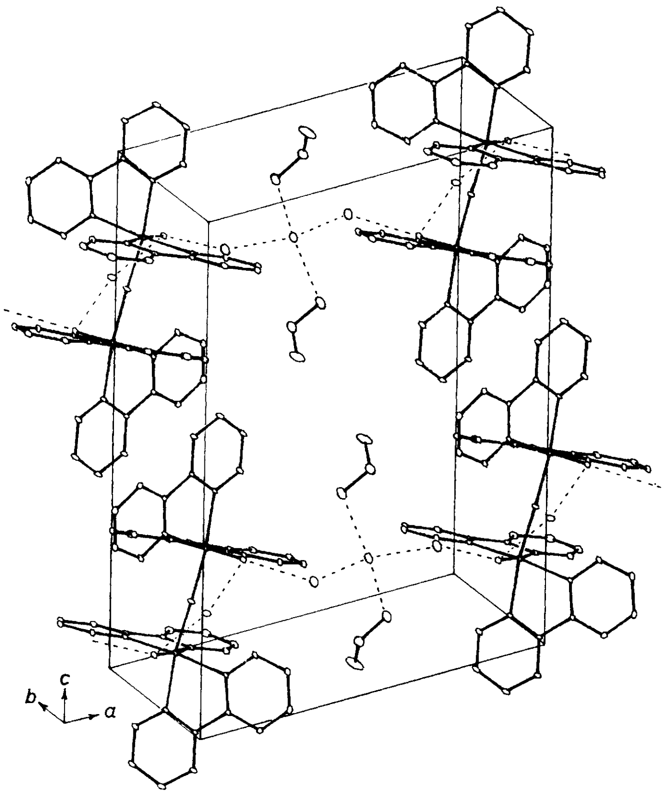

Figure 2. Unit cell of $[(bipy)_2FNi-F-NiF(bipy)_2]F{\cdot}2EtOH{\cdot}3H_2O$ showing the hydrogen bonds

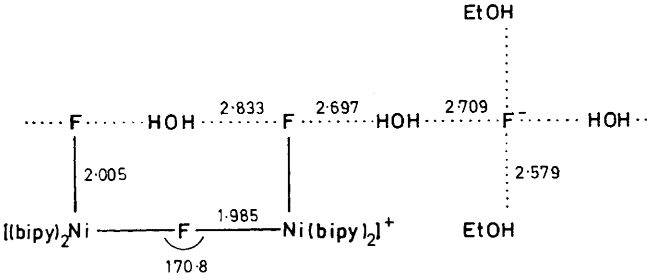

Figure 3. The three types of fluoride and four types of hydrogen bond of $[(bipy)_2FNi-F-NiF(bipy)_2]F{\cdot}2EtOH{\cdot}3H_2O$ [bond lengths in (Å), angles in (°)]

there are some nickel fluoride compounds whose crystal structures have been determined and these have R(Ni–F) = 2.022 and 1.981 Å (in NiF_2)[18] and 2.03(2) and 1.97(2) Å (in Ba_2NiF_6).[19] The Ni–F bond length of $[(bipy)_2FNi-F-NiF(bipy)_2]^+$ at 2.005(4) Å is in line with these values. Also it is very similar to that of the adjacent Ni–F bridge bond length of 1.985(3) Å. That the bridge bonds are slightly shorter than the terminal Ni–F bonds may be due to the internal hydrogen bonding within the complex (see below).

This compound is the first reported structure of a nickel complex with a single fluoride bridge. The nickel complex $[Ni_3L_6(NCS)_4F_2]$, where L is 3,5-diethyl-1,2,4-triazole, may also have single bridges since it is isomorphous with the cobalt(II) complex whose structure has been determined.[20] The complexes of general formula $[M_2(L-L)_4F_2]$ [M = Fe, Co, Cd, Mn, or Ni; L–L = bis(3,5-dimethylpyrazolyl)methane][21] and the NiL_2F_2 series of derivatives already mentioned[1] are thought to have double fluoride bridges.

Interest in fluoride bridges has centred on the angle at the fluoride. The nearer to linearity is the bridge the stronger is the π bonding between F and the metal atoms.[22] This being so, then the complex reported here with a bond angle of 170.8°, suggests a high degree of π bonding, which is consistent with the shorter R(Ni–F). The i.r. spectrum of $[(bipy)_2FNi-F-NiF(bipy)_2]F{\cdot}2EtOH{\cdot}3H_2O$ has a peak at 410 cm^{-1} which can be assigned to ν_{NiF}, and at 380 and 360 cm^{-1} which are the Ni–F–Ni bridge modes.[17,21]

The Hydrogen Bonds.—Within the cation, $[(bipy)_2FNi-F-NiF(bipy)_2]^+$, the structure is not staggered, as steric constraints would dictate, but the two Ni–F groups are on the same side of the complex and oriented at an angle of 65° to each other. The formation of hydrogen bonds by these Ni–F groups to the same water molecule may be partly responsible. Yet the hydrogen bonds are weak as shown by their $R(F \cdots O)$ value which is 2.833 Å. This is only marginally shorter than the sum of the van der Waals radii of F (1.40 Å) and O (1.50 Å)[23] and the hydrogen bonding is therefore classed as weak.[24] In addition, each ligand fluoride forms a second hydrogen bond to a water molecule in the lattice, Figure 3. These water molecules in turn are part of the solvent sphere around the anion, F^-. These bonds, with $R(NiF \cdots O)$ = 2.697 Å and $R(F^- \cdots O)$ = 2.709 Å, are marginally stronger. However, all the hydrogen bonds to water molecules are basically weak, as shown by the very broad i.r. bands at 3 375 (ν_{FHO}), 1 672 (δ_{FHO}), and *ca.* 600 cm^{-1} (γ_{FHO}).

The other components of the fluoride solvent sphere are ethanol molecules. There is, in the literature, an example of fluoride-to-ethanol hydrogen bonding. This exists in crystals of a copper complex, $[Cu(PPh_3)_3F]{\cdot}2EtOH$, in which the ligand fluoride is hydrogen bonded to two ethanol molecules with $R(F \cdots O)$ distances of 2.63 and 2.60 Å.[25] The noteworthy feature of this complex was not its hydrogen bonding, however, but the fact that it provided conclusive proof of Cu^IF.

In our nickel complex the fluoride-to-ethanol hydrogen bonding is shorter, 2.579 Å, which can be attributed to the formal charge on the fluoride. This is one of the shortest hydrogen bonds between fluoride and a non-acidic hydrogen bond donor. It is longer than that calculated by *ab initio* methods (2.39 Å) for the fluoride–methanol combination.[26] That it is longer can be attributed to each fluoride acting as an acceptor to *four* hydrogen bonds, which is an asynergic situation. The hydrogen bonds to ethanol are 0.12 Å shorter than those to water and this is to be expected from the relative hydrogen-bond energies of these molecules towards this ion: $E(F^- \cdots H_2O)$ = 97 and $E(F^- \cdots HOEt)$ = 132 kJ mol^{-1} (measured in the gas phase).[27]

If the $F^- \cdots HOEt$ bonding is strong then it should display its strength in the i.r., and indeed a broad band at 2 328 cm^{-1} is assigned to its ν_{FHO} mode, with possible bands at 795 and *ca.* 500 cm^{-1} for the bending modes. The species $[F(EtOH)_2(H_2O)_2]^-$ can be compared to $[F(H_2O)_4]^-$ in which $R(F \cdots O)$ = 2.634 and 2.687 Å.[5] The former may even be slightly more stable than the latter, the average $F \cdots O$ distances being 2.644 and 2.661 Å respectively. Were $[F(EtOH)_2(H_2O)_2]^-$ to be more stable in solution then this might explain some of the puzzling behaviour of fluoride ions in aqueous and non-aqueous alcoholic solutions.[28–32]

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References

1 S. J. Higgins and W. Levason, *Inorg. Chim. Acta*, 1986, **113**, 47.
2 S. L. Edwards, T. L. Poulos, and J. Krant, *J. Biol. Chem.*, 1984, **259**, 12984.

3 J. Emsley, M. Arif, P. A. Bates, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 2397 and refs. therein.

4 J. Emsley, M. Arif, P. A. Bates, and M. B. Hursthouse, *Inorg. Chim. Acta*, 1988, **154**, 17.

5 J. Emsley, M. Arif, P. A. Bates, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1988, 1387.

6 B. V. Bukvetsky, S. A. Polishchuk, and V. I. Simonov, *Kristallografiya*, 1973, **18**, 956.

7 M. L. H. Green, G. Parkin, C. Mingqin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 1400.

8 N. E. Dixon, R. L. Blakely, and B. Zenner, *Can. J. Biochem.*, 1980, **58**, 481.

9 W. Merts (ed.), 'Trace Elements in Human and Animal Nutrition,' 5th edn., Academic Press, San Diego, 1987, vol. 1, ch. 8.

10 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

11 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

12 G. M. Sheldrick, SHELX 86, Program for Crystal Structure Solution, University of Göttingen, 1986.

13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination and Refinement, University of Cambridge, 1976.

14 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

15 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

16 L. Sacconi, F. Mani, and A. Bencini, in 'Comprehensive Co-ordination Chemistry,' ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, ch. 50.

17 J. Reedijk and R. W. M. ten Hoedt, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 49.

18 W. H. Bauer, *Acta Crystallogr.*, 1958, **11**, 488.

19 H. G. von Schnering, *Z. Anorg. Allg. Chem.*, 1967, **353**, 13.

20 F. J. Rietmeijer, G. A. van Albada, R. A. G. de Graaft, J. G. Haasnoot, and J. Reedijk, *Inorg. Chem.*, 1985, **24**, 3597.

21 F. J. Rietmeijer, J. G. Haasnoot, A. J. Den Hartog, and J. Reedijk, *Inorg. Chim. Acta*, 1986, **113**, 147.

22 A. J. Edwards, in 'Comprehensive Co-ordination Chemistry,' ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, ch. 18, p. 680.

23 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

24 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

25 D. J. Gulliver, W. Levason, and M. Webster, *Inorg. Chim. Acta*, 1981, **52**, 153.

26 J. Emsley, R. J. Parker, and R. E. Overill, *J. Chem. Soc., Faraday Trans. 2*, 1983, 1347.

27 J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.*, 1983, **105**, 2944.

28 A. Allerhand and P. von Rague Schleyer, *J. Am. Chem. Soc.*, 1963, **85**, 1288.

29 S. E. Jackson, I. M. Strauss, and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1977, 174.

30 I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1977, 1796; *ibid.*, 1978, 2146.

31 A. J. Pasztor and C. M. Criss, *J. Solution Chem.*, 1977, **7**, 174.

32 A. Bhattachraya, K. Das, A. K. Das, and K. K. Kundu, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2194.

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