

The Crystal and Molecular Structure of the Tetraphenylphosphonium Salt of Pentacyanoferrate(III)- μ -Cyano-Tetracyanomonoammineferrate(III), $[(CN)_5FeNCFe(CN)_4NH_3]^{4-}$

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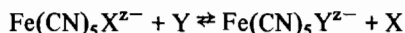
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The binuclear complex $Fe(CN)_{10}NH_3^{4-}$ has been prepared by combining solutions of $Fe(CN)_6^{3-}$ and $Fe(CN)_5NH_3^{2-}$. Crystals of the tetraphenylphosphonium salt are paramagnetic with $\mu = 3.54$ BM at 300 K. The crystal structure of this compound has been determined and refined to $R = 0.077$. The crystals are triclinic, one formula unit of $[(C_6H_5)_4P]_4 \cdot [Fe_2(CN)_{10}NH_3] \cdot 6H_2O$ is contained in the unit cell with $a = 12.828(5)$, $b = 14.214(8)$, $c = 14.148(5)$ Å, $\alpha = 92.66(4)$, $\beta = 103.72(3)$, $\gamma = 104.14(4)^\circ$, $d_{exp} = 1.285$ g cm $^{-3}$, $d_{calcd} = 1.282$ g cm $^{-3}$, space group $P1$. The structure contains $[(NC)_5FeNCFe(CN)_4NH_3]^{4-}$ complexes loosely connected by hydrogen bonds along the c -axis. Average distances are: $Fe-C = 1.93$ Å, $C-N = 1.17$ Å, $Fe-NC = 1.90$ Å, $Fe-NH_3 = 2.08$ Å. The two iron atoms are linked by an almost linear cyanide bridge with an ecliptic conformation of the two different FeC_5-N units. Mössbauer spectra demonstrate the presence of two similar but distinct coordination environments.

Introduction

Cyano complexes of iron in its two- and three-valent state as well as their substitution derivatives have been the subject of many investigations since the early times of coordination chemistry. Many studies were concerned with the kinetics of the substitution reaction



and corresponding redox processes. The vast amount of experimental work has recently been reviewed by Sharpe [1]. For the special case of the aquo complex, $Fe(CN)_5H_2O^{2-}$, the formation of a binuclear species $Fe_2(CN)_{10}^{4-}$ has been postulated [1, 2]. Its structure

has been assumed to contain two cyanide bridges. This stereochemically rather improbable structural hypothesis, however, has apparently never been tested by an X-ray structure analysis of a crystalline compound. The dimerisation of $Fe(CN)_6^{4-}$ and $Fe(CN)_5NH_3^{2-}$ leads to the mixed-valence complex bridged by one cyano group [3], presumably by the substitution of the ammonia ligand by one nitrogen end of the ferrocyanide ion. This assumption was based on the extremely slow ligand exchange of $Fe(CN)_6^{4-}$ [1]. The oxidized and reduced forms of the binuclear cyano complex were generated in a spectroelectrochemical experiment [3]. In particular the Fe(III)-Fe(III) complex showed a visible spectrum very similar to the one attributed to the ion $Fe_2(CN)_{10}^{4-}$. We therefore decided to investigate this system more closely with the aim to grow single crystals suitable for an X-ray study in order to distinguish between a singly or doubly bridged arrangement.

The structural and magnetic properties of hydroxo- and oxo-bridged iron dimers with both metal ions in the high spin state have been thoroughly investigated [4]. The structure of the binuclear iron cyano complex discussed in this paper presents to our knowledge the first case where both iron ions are in the low spin state.

Crystal Structure

A crystal of $[(C_6H_5)_4P]_4[Fe_2(CN)_{10}NH_3] \cdot 6H_2O$ having the shape of an almost isometric parallelepiped of dimensions $0.35 \times 0.30 \times 0.30$ mm was mounted on a Syntex P2₁ diffractometer. Originally, the composition was assumed to be $[(C_6H_5)_4P]_4H[Fe_2(CN)_{11}] \cdot 6H_2O$ (cf. Experimental). The unit cell was

determined from 15 carefully centered reflections to be triclinic with lattice dimensions $a = 12.828(5)$, $b = 14.214(8)$, $c = 14.148(5)$ Å, $\alpha = 92.66(4)$, $\beta = 103.72(3)$, and $\gamma = 104.14(4)^\circ$. This unit cell is based on the three shortest translations. MoK α radiation (graphite monochromator) with a wavelength of 0.71069 Å was used. The cell contains one formula unit, $d_{\text{exp}} = 1.285(9)$ g cm $^{-3}$, $d_{\text{calcd}} = 1.282$ g cm $^{-3}$.

The intensities of 3423 independent reflections were measured up to $\sin \theta/\lambda = 0.435$ Å $^{-1}$ using MoK α radiation. 515 reflections were below the 3σ limit, 814 below the 6σ limit. Specifications for data collection and the calculation of the standard deviation σ are given in ref. [5]. No significant change of the intensities of three periodically measured check reflections could be observed. Data reduction included Lorentz- and polarization correction but no correction for absorption ($\mu(\text{MoK}\alpha) = 4.42$ cm $^{-1}$). Scattering factors for the neutral atoms were taken from Cromer and Mann [6], and anomalous dispersion factors for Fe and P from Cromer [7].

Data reduction, Patterson maps, and the direct method program MULTAN were carried out on a PDP 11/45 at Stanford University. All the other calculations were made using the CDC CYBER 70 of the University of Lausanne with programs taken from the X-RAY 72 system (modified version of D. Schwarzenbach).

The E-statistics presented strong evidence for a centrosymmetric space group. The calculations were therefore performed in $P\bar{1}$, assuming the center (or pseudo-center) of symmetry in the middle of the line joining the two iron atoms. Since a Patterson map did not reveal the sites of the iron and phosphorus atoms, the direct methods program MULTAN was used. 397 normalized structure factors produced 32 different phase sets. The set with an absolute figure of merit of 1.135 gave trial positions for iron and phosphorus as well as some of the carbon atoms of the cyano complex. The remaining non-hydrogen atoms could be located by difference Fourier maps. Standard least-squares procedures were used for refining the structure, the phenyl rings being treated as rigid groups with a bondlength of 1.399 Å and an angle of 120° . Four oxygen atoms of the six water molecules could easily be located, two of which showed population factors smaller than unity. So far the centro-symmetric model was based on $\text{Fe}_2(\text{CN})_{11}$ dimer with the inversion center on the CN bridge disregarding thus the slight inequality of the X-ray scattering factors of the carbon and nitrogen atoms. The isotropic refinement assigning individual temperature factors gave a final R factor of 0.097. One of the terminal nitrogen atoms of the complex showed an unusually high isotropic temperature factor U of 0.18 compared to 0.05 for the other nitrogen atoms. Moreover, some of the rings could not be refined properly and showed some disorder. This was taken as an indication that a

non-centrosymmetric structure might be a better choice for the space group. The next calculations were therefore carried out in space group $P1$ and the cyanide ion with the abnormally high U value for N was replaced by NH_3 . Individual isotropic factors were assigned to the atoms of the binuclear complex, the phosphorus, and the oxygen atoms. A general temperature factor was given to all C-atoms of the rings. The binuclear complex is thus represented by the formula $\text{Fe}_2(\text{CN})_{10}\text{NH}_3^{4-}$, which is also consistent with chemical analysis (*vide infra*). The application of Hamilton's criterion [8] clearly demonstrated that the centro-symmetric model has to be rejected on the 0.1% level. First the complex was refined in four least-squares cycles using isotropic temperature factors and subsequently with the phenyl rings as rigid groups leading to an R of 0.079, the carbon atom of the bridging cyanide being kept fixed as a point of reference. The six oxygen atoms of the water molecules are now distributed among seven positions, four of them having an occupancy factor fixed at 0.75 on the basis of the Fourier map and least-squares refinement. Inverting the cyanide bridge, *i.e.* the conversion of $(\text{NC})_5\text{-Fe-NC-Fe}(\text{CN})_4\text{NH}_3^{4-}$ to $(\text{NC})_5\text{Fe-CN-Fe}(\text{CN})_4\text{NH}_3^{4-}$ did not affect the R factor. The temperature factor of the nitrogen atom of the bridge, however, was substantially higher for the latter structure of the complex. The structure is therefore described in terms of two FeC_5N units rather than in terms of the two very different groups FeC_6 and FeC_4N_2 . This assignment is strongly supported by the results of Mössbauer spectroscopy (*cf.* next section). The final least-squares treatment including all atoms gave $R = 0.077$ and $R_w = 0.090$. The introduction of anisotropic thermal motion for the atoms of the complex did not result in an improvement of the agreement. Final atomic parameters of the complex are listed in Table I. It should be noted that the standard deviations of the structural parameters are rather large. This is attributed to the fact that data collection could not be extended to high 2θ values. A list of F_{obs} , $\Delta F (= F_{\text{obs}} - F_{\text{cal}})$, and $\sigma(F_{\text{obs}})$ and a list of the parameters of the tetraphenylphosphonium groups are available as supplementary material. A difference Fourier map was calculated with these results. The highest peak, located at the site of one Fe atom corresponds to 15% of the density of a carbon atom. The remaining peaks were of the order of 10% and less of the carbon electron density. These peaks were in the close neighbourhood of the oxygen atoms and of the phenyl carbons. No attempt, however, was made to locate the 95 hydrogen atoms.

Description of the Structure

A stereo view of the unit cell of $[(\text{C}_6\text{H}_5)_4\text{P}]_4\text{-}[\text{Fe}_2(\text{CN})_{10}\text{NH}_3] \cdot 6\text{H}_2\text{O}$ is shown in Figure 1. The

TABLE I. Fractional Atomic Coordinates^a and Thermal Parameters^b for the Iron Complex, the Water Molecules, and the Phosphorus Atoms of the Title Compound.

Atom	X	Y	Z	U
Fe(1)	3976(5)	4724(4)	3251(4)	427(16)
Fe(2)	6018(5)	5264(4)	6821(4)	416(15)
C(11)	5283(29)	4980(25)	2773(25)	482(10)
N(12)	4574(29)	4990(26)	7309(26)	877(124)
C(21)	2630(22)	4488(19)	3681(19)	246(78)
C(22)	7300(42)	5472(35)	6390(34)	625(160)
C(31)	3117(26)	4456(23)	1959(24)	319(97)
C(32)	6839(34)	5610(31)	8160(34)	717(141)
C(41)	4056(27)	3382(26)	3231(24)	578(117)
C(42)	6019(22)	6590(21)	6727(20)	322(90)
C(51)	3913(23)	6058(23)	3251(21)	283(91)
C(52)	5969(28)	3933(28)	6843(26)	641(121)
N(61)	4798(14)	4964(13)	4585(12)	503(80)
C(62) ^c	5205	5050	5424	277(104)
N(11)	5922(18)	5144(15)	2261(17)	859(67)
N(21)	1890(21)	4371(18)	3992(18)	537(85)
N(22)	8192(25)	5582(21)	6213(21)	685(103)
N(31)	2478(17)	4216(14)	1135(15)	341(61)
N(32)	7262(26)	5776(22)	8951(25)	934(119)
N(41)	3955(24)	2565(23)	3435(21)	762(108)
N(42)	5863(20)	7373(19)	6763(18)	576(84)
N(51)	3933(26)	6817(26)	3277(23)	650(107)
N(52)	6097(27)	3070(28)	6817(24)	743(114)
O(11)	4859(18)	8302(16)	4985(16)	598(76)
O(12)	4995(18)	1718(16)	5013(17)	712(74)
O(21)	388(199)	3114(18)	98754(179)	1031(85)
O(22) ^d	973(2)	6860(18)	16(2)	740(81)
O(31) ^d	6060(23)	5906(21)	3497(210)	960(100)
O(32) ^d	4158(20)	4443(19)	977(2)	846(85)
O(42) ^d	3694(17)	3144(15)	8131(15)	1112(62)
P(1)	7496(9)	8434(83)	1241(8)	443(31)
P(2)	32(1)	7210(7)	3849(7)	332(26)
P(3)	2500(9)	9137(8)	8884(8)	412(29)
P(4)	971(1)	2795(9)	6314(8)	424(31)

^aCoordinates are $\times 10^4$. ^b $U \times 10^4$, the temperature factor has the form $\exp(-T)$ where $T = 8\pi^2 U(\sin\theta/\lambda)^2$. ^cPoint of reference. ^dPopulation factor is 0.75.

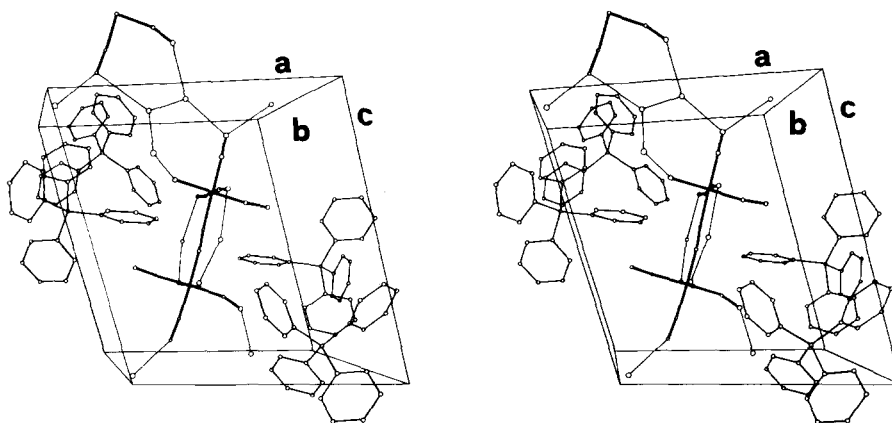
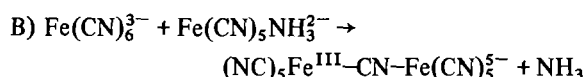
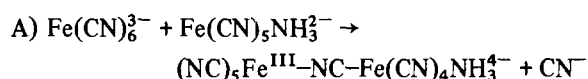


Fig. 1. Stereo view of the unit cell of the title compound. Heavy lines represent bonds within the complex, light lines indicate hydrogen bonds between complexes.

binuclear complexes are loosely linked by hydrogen bonds $CN \cdots H_2O \cdots NC$ and $CN \cdots H_2O \cdots H_2O \cdots H_3N$ along the c -axis. An ORTEP plot of the complex is presented in Figure 2. The two iron atoms are in the center of a distorted octahedron linked by one cyanide group. One iron is coordinated by five C(CN) atoms and one N(NC) atom, the other one again by five C(CN) and one N(NH₃) where the ammonia molecule is in a *cis*-position to the bridge. The two moieties of the binuclear complex are oriented in such a way that an eclipsed conformation is realized. Table II contains a list of important bond lengths and angles, a comparison with corresponding data of related structures is given in Table III.

Despite the rather large standard deviations of the atomic parameters and hence of the interatomic distances the solution of the structure of $[(C_6H_5)_4P]_4[Fe_2(CN)_{10}NH_3] \cdot 6H_2O$ unambiguously demonstrates the presence of only one cyanide bridge. Whether a rearrangement to the postulated doubly bridged species is occurring in solution can, of course, not be determined from our structural study.

The presence of an ammonia molecule coordinated to one of the iron atoms is a very interesting point as far as the chemical reaction of formation of the binuclear species is concerned. The dimerization certainly involves the substitution of a cyanide ligand of the $Fe(CN)_6^{3-}$ ion (equation A). The customary view of such reactions (equation B) which implies the substitution of the ammonia molecule of $Fe(CN)_5NH_3^{2-}$ has to be rejected as the pathway of formation of our binuclear complex.



Whereas the first-order rate constant for dissociation of $Fe(CN)_6^{3-}$ has been determined as 6×10^{-7}

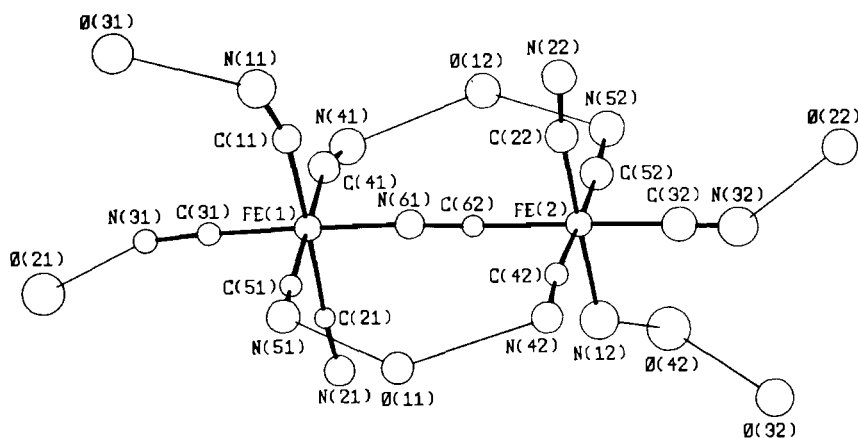
Figure 2. ORTEP plot of $\text{Fe}_2(\text{CN})_{10}\text{NH}_3^{4-}$ together with oxygen atoms of water molecules attached to the complex by hydrogen

TABLE II. Selected Bond Distances (Å) and Angles (deg) in the Title Compound.

Fe(1)–C(11)	1.91(4)	Fe(2)–N(12)(NH ₃)	2.08(4)
Fe(1)–C(21)	1.93(3)	Fe(2)–C(22)	1.85(6)
Fe(1)–C(31)	1.86(3)	Fe(2)–C(32)	1.91(4)
Fe(1)–C(41)	1.93(4)	Fe(2)–C(42)	1.90(3)
Fe(1)–C(51)	1.92(3)	Fe(2)–C(52)	1.88(4)
Fe(1)–N(61)(NC)	1.90(2)	Fe(2)–C(62)	1.97(1)
Fe(1)–Fe(2)	5.034(8)		
C(11)–N(11)	1.21(5)	C(62)–N(61)	1.16(2)
C(21)–N(21)	1.12(4)	C(22)–N(22)	1.20(7)
C(31)–N(31)	1.23(4)	C(32)–N(32)	1.11(5)
C(41)–N(41)	1.19(5)	C(42)–N(42)	1.18(4)
C(51)–N(51)	1.07(5)	C(52)–N(52)	1.28(7)
N(11)–O(31)	2.99(4)	N(12)–O(42)	3.01(4)
N(31)–O(21)	2.87(3)	N(32)–O(22)	3.18(4)
N(41)–O(12)	2.80(4)	N(42)–O(11)	3.06(3)
N(51)–O(11)	2.94(4)	N(52)–O(12)	2.95(4)
O(31)–O(32)	2.71(4)	O(42)–O(32)	2.74(4)
Fe(1)–C(62)–Fe(2)	179.3(0.2)	Fe(1)–N(61)–Fe(2)	176.1(0.9)
C(31)–Fe(1)–N(61)	177.6(1.2)	C(32)–Fe(2)–C(62)	174.2(1.4)

TABLE III. Comparison of Selected Bond Lengths (Å).

	Fe–C	C–N	Fe–N	Reference
$\text{K}_3\text{Fe}(\text{CN})_6$	1.93, 1.95, 1.97	1.13, 1.17	–	a
$\text{Cs}_2\text{LiFe}(\text{CN})_6$	1.93	1.15	–	b
$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 2\text{H}_2\text{O}$	1.89, 1.93, 1.94	1.14, 1.17	2.01	c
Title complex	1.93	1.17	1.90, 2.08	This Work

^aN. G. Vannerberg, *Acta Chem. Scand.*, 26, 2863 (1972).

^bB. I. Swanson and B. R. Ryan, *Inorg. Chem.*, 12, 286 (1973).

^cA. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, A 28, 340 (1974).

s^{-1} [1] no corresponding figure appears to be known for the dissociation of NH_3 in $\text{Fe}(\text{CN})_5\text{NH}_3^{2-}$. Since our structural results are opposed to the assumption usually made in kinetic studies of substituted cyanoferrates, further experimental evidence was looked

for. The most direct probe for the atoms directly bonded to iron is obviously Mössbauer spectroscopy. In particular a clear distinction of two FeC_5N (case A) versus one FeC_6 and one FeC_4N_2 (case B) coordination units is expected from the results of this

technique. Moreover the two inequivalent nitrogen atoms (one from NH_3 , one from NC) should show up in two different sets of Mössbauer parameters. Two FeC_5N moieties would also be the relevant coordination units in the symmetric doubly bridged species $Fe_2(CN)_{10}^{4-}$. In this case, however, both compounds of the binuclear complex should produce the same Mössbauer spectrum. The Mössbauer spectrum of $[(C_6H_5)_4P]_4[Fe(CN)_{10}NH_3] \cdot 6H_2O$ from the same batch as the crystal consists of two distinct doublets of the same intensity corresponding to two different FeC_5N units [9]. The chemical shifts (relative to natural iron) are $-0.73(3)$ and $-0.067(3)$ $mm\ s^{-1}$, the quadrupole splittings $1.92(3)$ and $1.11(3)$ $mm\ s^{-1}$ being in good agreement with corresponding results of $Fe(III)(CN)_5L$ complexes [10]. The first doublet is tentatively assigned to the FeC_5NH_3 unit, the second one to the FeC_5NC moiety by comparison with spectra of related mononuclear complexes [9, 10].

The magnetic susceptibility of $[(C_6H_5)_4P]_4[Fe_2(CN)_{10}NH_3] \cdot 6H_2O$ obeys the Curie-Weiss law $\chi = C/(T - \theta)$ in the temperature range 100–300 K with a Weiss constant of -104 K. At 300 K the effective magnetic moment is 3.54 BM for the binuclear compound corresponding to an average moment of 2.50 BM per FeC_5N unit. This value compares with the 2.25 BM of $K_3Fe(CN)_6$ indicating that the paramagnetism of the binuclear complex also contains a considerable amount of orbital contribution (spin only: 1.73 BM). Below 100 K, the susceptibility deviates strongly from Curie-Weiss behavior. These deviations may be due to a structural phase change occurring at about 40 K.

Experimental

303 mg (1 mmol) of $Na_2[Fe(CN)_5NH_3] \cdot 3H_2O$ and the equimolar amount of 329 mg of $K_3Fe(CN)_6$ are dissolved in 10 ml of bidistilled water and kept in the dark for 5 hr. This solution is added dropwise to a solution of 1.87 g (5 mmol) of tetraphenylphosphonium chloride in a mixture of 30 ml water and 10 ml ethanol. Slow evaporation of this purple solution produced dark olive-green crystals of the binuclear complex.

Analytical data:

	Found	Calc. for I	Calc. for II
Fe	6.05	5.99	6.02
P	6.78	6.64	6.68
C	68.42	68.92	68.65
N	8.31	8.26	8.31
H	5.12	5.14	5.16

Originally it was assumed that this reaction leads to $Fe_2(CN)_{11}^{5-}$ by substitution of the ammonia molecule. Since only four phosphorus were found per two iron the missing positive charge was attributed to an additional proton. The presence of protons in phosphonium salts of cyanoferrates is not too uncommon [11]. The stoichiometry first assigned was therefore $[(C_6H_5)_4P]_4H[Fe_2(CN)_{11}] \cdot 6H_2O$ (I) whereas the crystal structure analysis showed the correct formula to be $[(C_6H_5)_4P]_4[Fe_2(CN)_{10}NH_3] \cdot 6H_2O$ (II). Subsequent direct determination of ammonia by distillation and titration gave 0.97 ammonia molecules per two irons in agreement with formula II.

Fe was determined colorimetrically as $Fe(phen)_3^{2+}$, the absence of Na and K was verified by atomic absorption spectroscopy. P, C, N, and H analyses were performed by the Analytical Laboratory of CIBA-GEIGY in Basel.

Acknowledgments

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References

- 1 A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press (1976).
- 2 A. D. James, W. C. E. Higginson and R. S. Murray, *J. Chem. Research (M)*, 1084 (1977).
- 3 R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler and F. Wenk, *J. Am. Chem. Soc.*, **95**, 8457 (1973).
- 4 H. J. Schugar, G. R. Rossman, C. G. Barraclough and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 2683 (1972); J. A. Thich, C. C. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza and H. J. Schugar, *ibid.*, **98**, 1425 (1976); C. C. Ou, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *ibid.*, **100**, 2053 (1978).
- 5 M. A. Bobrik, K. O. Hodgson and R. H. Holm, *Inorg. Chem.*, **16**, 1851 (1977).
- 6 D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A 24**, 321 (1968).
- 7 D. T. Cormer, *Acta Cryst.*, **18**, 17 (1965).
- 8 W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).
- 9 F. J. van Steenwijk and P. Roder, *Helv. Phys. Acta*, in press.
- 10 N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London (1971).
- 11 S. Papp, S. Kovács and I. Liszi, *J. Inorg. Nucl. Chem.*, **34**, 3111 (1972).