Salts of the Tris(violurato)ferrate(II) Ion: Crystal Structure of Ammonium Tris(violurato)ferrate(II) Hydrate

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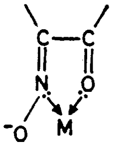
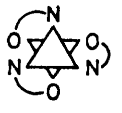
Salts of the type $M^+[FeV_3]^- \cdot xH_2O$ have been prepared (where M^+ = alkali-metal cation, V^- = violurate) and found to be diamagnetic.

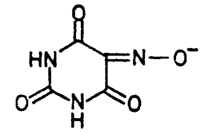
The crystal structure of the title compound $[NH_4][FeV_3] \cdot$ *ca.* $4.5H_2O$ has been determined by *X*-ray diffraction and refined by least squares to *R* 0.07 for 3 868 observed reflections. Crystals are triclinic, space group $P\bar{1}$, a = 16.242(3), b = 15.690(3), c = 9.848(2) Å, α = 90.95(2), β = 106.99(2), γ = 74.20(2)°, Z = 4. There are two independent cations and anions in the asymmetric unit; the geometry of the anion co-ordinated by three bidentate violurate ligands ($V^- = C_4O_4N_3H_2^-$) is *fac* (means: Fe–O 1.98_3, Fe–N 1.87_7 Å), and closely resembles that found in ferroverdin. The accuracy of the structure is inhibited by serious disorder among the solvent molecules in the lattice.

RELATIVELY little work has been carried out on complexes of organic nitroso-ligands with transition-metal ions, and this has been almost entirely concerned with ligands of the *o*-nitrosophenolate or isonitrosoketone type. The little available structural data shows the formation of a five-membered chelate ring with the metal by way of the carbonyl oxygen and nitrogen lone-pair, the disposition of the ligands about the metal in tris-chelate derivatives being *fac*.[1,2] Derivatives of these ligands may be considered as ' isoelectronic ' with complexes of ligands such as 8-hydroxyquinoline which have been much more widely studied, although structural data are sparse on that system also.





Among the more widely studied ligands of this type is the violurate anion, V^-; salts of the type $FeL_2 \cdot xH_2O$ were prepared for a variety of ligands L^- (including V^-) with iron(II) by Cambi and his co-workers.[3,4] We report here the preparation of salts of the type $M^+[FeV_3]^- \cdot xH_2O$ where M^+ is an alkali-metal cation, and the determination of the crystal structure of the ammonium salt. The violurate anion may be formally represented as (I) $C_4H_2N_3O_4^-$:



(I)

EXPERIMENTAL

For $M = [NH_4]^+$, K^+, Rb^+, and Cs^+, derivatives $M[FeV_3] \cdot xH_2O$ are easily prepared as deep blue finely crystalline solids with a bronze sheen by cooling a hot concentrated aqueous solution of excess of MV with iron(II) sulphate. The Na^+ and Li^+ derivatives are very soluble and to obtain pure crystalline solids it is necessary in these cases to use iron(II) perchlorate and water–ethanol (1 : 1) solutions. Analytical data suggest the following values for x: Li^+ 4, Na^+ 4, K^+ 3.5, Rb^+ 4, Cs^+ 3.5, and $[NH_4]^+$ 4.5 (Table 1). The complexes are diamagnetic.

TABLE 1

Typical analytical results for the violurate derivatives; calculated values are given in parentheses below those found

Compound	C	N	H	Fe	M+
KV	20.51	17.49	2.72		17.16
	(20.78)	(18.18)	(2.60)		(16.88)
$Li[FeV_3] \cdot 4H_2O$	24.45	20.44	2.34	10.11	
	(23.89)	(20.90)	(2.34)	(9.26)	
$Na[FeV_3] \cdot 4H_2O$	23.33	20.64	2.14	9.37	4.04
	(23.28)	(20.36)	(2.28)	(9.05)	(3.72)
$K[FeV_3] \cdot 3.5H_2O$	23.07	19.98	2.20	8.40	
	(23.02)	(20.13)	(2.09)	(8.92)	
$Rb[FeV_3] \cdot 4H_2O$	21.02	18.24	2.22	8.40	
	(21.40)	(18.50)	(2.07)	(8.20)	
$Cs[FeV_3] \cdot 3.5H_2O$	20.02	17.22	1.73	7.74	
	(20.02)	(17.51)	(1.82)	(7.78)	
$[NH_4][FeV_3] \cdot 4.5H_2O$	23.35	22.60	2.77	8.80	
	(22.80)	(22.61)	(3.17)	(8.83)	

The Mössbauer spectra were recorded with a scanned velocity spectrometer operating in the time mode at 77, 195, and 295 K, by use of a 10 mCi ^{57}Co source in palladium foil. Samples were always powdered and supported in a 3 cm diameter Perspex holder such that the sample

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[1] P. W. Carreck, J. Charalambous, M. J. Kensett, M. McPartlin, and R. Sims, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 749.

[2] S. Candeloro, D. Grdenić, N. Taylor, B. Thompson, M. Viswamitra, and D. Crowfoot Hodgkin, *Nature*, 1969, **224**, 589.

[3] L. Cambi, *IX. Congr. Internat. Quim. Pura Apl.*, 1934, **2**, 199.

[4] L. Cambi and A. Cagnasso, *Gazzetta*, 1933, **63**, 767.

contained *ca.* 10 mg Fe cm^{-2}. Details of the spectra are recorded in Table 2; errors are typically ± 0.03 mm s^{-1}.

Complexes of the type M[FeV$_3$] crystallize readily, those of the [NH$_4$]$^+$, Na$^+$, K$^+$, and Rb$^+$ salts being of a size usable for *X*-ray work. However, of these, the Na$^+$ salt gave a poor diffraction pattern and the unit cell of the K$^+$ derivative proved excessively large. Although the crystals of the Rb$^+$ were larger than those of the [NH$_4$]$^+$ derivative, the latter was chosen for study because of the lack of heavy atoms other than the iron, which it was hoped would lead to a reasonable definition of the anion-core geometry; this hope was not fully realized, partly because the crystals were rather small and the data correspondingly weak and limited, but chiefly because of the presence of appreciable disorder in the lattice.

TABLE 2

Isomer shifts and quadrupole splittings derived from the Mössbauer spectra (mm s^{-1})

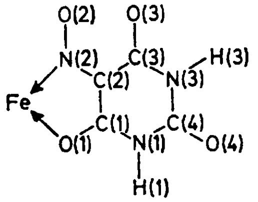
	T/K					
	298		195		72	
	ΔEq	δ	ΔEq	δ	ΔEq	δ
Li[FeV$_3$]·4H$_2$O	0.34	0.49	0.45	0.51	0.37	0.54
Na[FeV$_3$]·4H$_2$O	0.26	0.43	0.37	0.54	0.49	0.52
K[FeV$_3$]·3.5H$_2$O	0.26	0.49	0.34	0.52	0.37	0.54
Rb[FeV$_3$]·4H$_2$O	0.43	0.50	0.45	0.54	0.51	0.57
Cs[FeV$_3$]·3.5H$_2$O	0.37	0.49	0.45	0.54	0.51	0.57
[NH$_4$][FeV$_3$]·4.5H$_2$O	0.30	0.50	0.41	0.52	0.45	0.54

A crystal, a cuboid *ca.* 0.10 mm, was used for the crystallographic work. Unit-cell dimensions were obtained from a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer; a unique data set was gathered by conventional 2θ—θ scan in the range $2\theta < 40°$ yielding 4 314 independent reflections of which 3 868 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement. No absorption correction was necessary.

Crystal Data.—[NH$_4$][Fe(C$_4$O$_4$N$_3$H$_2$)$_3$]·4.5H$_2$O, C$_{12}$H$_{19}$FeN$_{10}$O$_{16.5}$, $M = 623.2$, Triclinic, $a = 16.242(3)$, $b = 15.690(3)$, $c = 9.848(2)$ Å, $\alpha = 90.95(2)$, $\beta = 106.99(2)$, $\gamma = 74.20(2)°$, $U = 2\,304(1)$ Å^3, $D_m = 1.78(1)$ g cm^{-3}, $Z = 4$, $D_c = 1.80$ g cm^{-3}, $F(000) = 1\,276$. Mo-K_α radiation (monochromatic) $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 3.86 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2). Neutral-atom scattering factors, that for Fe corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[5-7]

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares, the parameters of the FeN$_3$O$_3$ anion cores being refined jointly in order to approximate to a full-matrix process; anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$ were employed for non-hydrogen atoms. Hydrogen atoms attached to the ligands were located and their positional parameters refined with isotropic thermal parameters $U = 0.05$ Å^2. Among the solvent water molecules serious disorder exists: O(1)–(8) are well ordered, but their thermal motion is high; O(9) and O(10) each appear to be distributed over two sites, and their populations were determined from a difference map. In view of the high thermal motion and disorder among the solvent molecules, with corresponding nonlocation of the associated hydrogen atoms it has not been possible to make an assignment of the cations; consideration of the neighbouring geometry about each ' oxygen ' was fruitless because of the proximity of disorder. Refinement converged at R 0.074, R' [$= (\Sigma w||F_o| - F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] 0.086, a weighting scheme of the form $w = [\sigma^2(F_o) + 10^{-4}n(F_o)^2]^{-1}$ being found appropriate for $n = 3$.

Atomic numbering within the ligand is as follows: O(1) and N(2) within each ligand chelate the iron; where necessary each atom is preceded by *ij* denoting the anion (*i*) and ligand *j* (1—3) within the anion.



Computation was carried out on the local CDC 6200 machine using a variant of the ' *X*-Ray '72 ' program system.[7] Structure-factor tables are deposited as Supplementary Publication No. SUP 21730 (26 pp., 1 microfiche) * together with detailed ligand geometries, least-squares planes, and anisotropic thermal parameters.

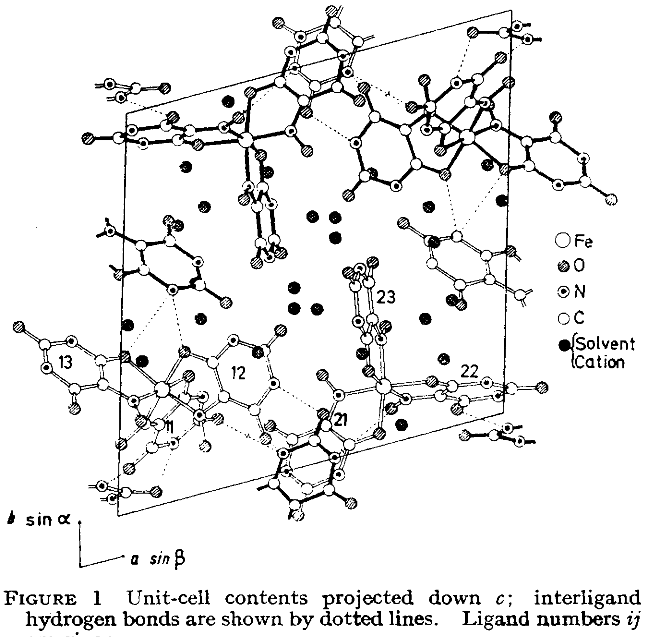


FIGURE 1 Unit-cell contents projected down *c*; interligand hydrogen bonds are shown by dotted lines. Ligand numbers *ij* are given

DISCUSSION

As expected, the structure is comprised of [FeV$_3$] species, presumably anions, together with associated lattice water molecules (Figure 1), there being two

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* For details, see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **19**, 17.

[7] ' *X*-Ray System,' Technical Report TR 192, of the Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

TABLE 3

Atomic fractional cell co-ordinates (x,y,z) ($\times 10^3$ for H $\times 10^4$ others) and thermal parameters ($\times 10^3$ Å^2). Least-squares estimated standard deviations in the final digit are given in parentheses

Atom	x	y	z
Anion (1)			
Fe	1 087(1)	2 876(1)	0 566(2)
Ligand (1)			
O(1)	1 780(5)	3 029(5)	−0 713(7)
N(1)	2 150(5)	2 421(5)	−2 645(9)
C(1)	1 681(6)	2 508(7)	−1 686(11)
O(2)	0 043(5)	1 787(5)	−0 822(8)
N(2)	0 652(5)	2 141(6)	−0 810(9)
C(2)	1 030(6)	2 026(7)	−1 876(10)
O(3)	0 265(5)	1 119(5)	−3 401(7)
N(3)	1 401(5)	1 456(6)	−3 924(9)
C(3)	0 857(6)	1 502(7)	−3 087(11)
C(14)	2 071(7)	1 868(8)	−3 748(11)
O(4)	2 552(5)	1 765(5)	−4 506(8)
H(1)	275(7)	279(7)	−752(12)
H(3)	136(7)	104(7)	−530(12)
Ligand (2)			
O(1)	1 650(4)	3 659(4)	1 894(7)
N(1)	2 926(6)	3 617(6)	3 680(9)
C(1)	2 398(7)	3 208(7)	2 711(11)
O(2)	2 244(5)	1 167(5)	1 394(8)
N(2)	2 081(5)	1 979(5)	1 599(9)
C(2)	2 711(6)	2 277(7)	2 613(11)
O(3)	3 811(4)	0 951(5)	3 745(8)
N(3)	3 993(5)	2 269(5)	4 489(9)
C(3)	3 512(6)	1 750(6)	3 604(10)
O(4)	4 152(5)	3 541(5)	5 543(8)
C(4)	3 736(6)	3 160(7)	4 660(11)
H(1)	271(7)	411(7)	387(12)
H(3)	440(7)	189(7)	512(12)
Ligand (3)			
O(1)	0 089(4)	3 936(5)	−0 375(7)
N(1)	−1 309(5)	4 680(6)	−0 305(10)
C(1)	−0 533(7)	4 004(7)	0 154(12)
O(2)	0 553(3)	2 229(5)	2 694(8)
N(2)	0 347(5)	2 774(5)	1 648(9)
C(2)	−0 466(7)	3 398(8)	1 260(11)
O(3)	−1 199(5)	2 984(6)	2 797(9)
N(3)	−1 950(6)	4 182(6)	1 251(11)
C(3)	−1 201(7)	3 471(8)	1 846(13)
O(4)	−2 712(5)	5 400(6)	−0 249(6)
C(4)	−2 013(7)	4 775(7)	0 237(14)
H(1)	−128(7)	508(7)	−084(12)
H(3)	−261(7)	419(7)	161(12)
Anion (2)			
Fe	6 863(1)	1 456(1)	2 593(2)
Ligand (1)			
O(1)	6 776(4)	0 308(5)	3 280(7)
N(1)	5 744(5)	−0 443(6)	3 107(9)
C(1)	6 000(6)	0 241(7)	2 698(11)
O(2)	5 260(3)	2 147(5)	0 439(9)
N(2)	5 696(6)	1 539(6)	1 380(9)
C(2)	5 375(6)	0 869(7)	1 642(10)
O(3)	3 925(5)	1 241(5)	−0 087(8)
N(3)	4 376(5)	−0 004(6)	1 368(9)
C(3)	4 505(6)	0 755(7)	0 881(11)
O(4)	4 701(5)	−1 177(5)	2 947(8)
C(4)	4 913(7)	−0 579(7)	2 503(12)
H(1)	606(7)	−073(7)	393(12)
H(3)	392(7)	−019(7)	107(12)
Ligand (2)			
O(1)	8 116(4)	1 258(4)	3 853(7)
N(1)	9 551(5)	0 856(5)	3 765(9)
C(1)	8 646(6)	1 005(6)	3 137(10)
O(2)	7 070(4)	0 856(5)	−0 040(7)
N(2)	7 441(5)	0 999(5)	1 221(9)
C(2)	8 346(6)	0 848(6)	1 685(10)
O(3)	8 783(4)	0 399(5)	−0 394(7)
N(3)	9 850(5)	0 448(6)	1 644(9)
C(3)	8 966(6)	0 559(7)	0 870(11)
O(4)	10 988(4)	0 365(5)	3 712(8)
C(4)	10 196(7)	0 550(7)	3 081(11)
H(1)	975(7)	098(7)	463(12)
H(3)	1 022(7)	032(7)	133(12)
Ligand (3)			
O(1)	6 461(5)	1 942(5)	4 232(8)
N(1)	6 166(6)	3 240(6)	5 300(9)
C(1)	6 397(7)	2 759(7)	4 229(11)
O(2)	6 878(5)	2 943(5)	1 063(8)
N(2)	6 769(5)	2 647(5)	2 140(9)
C(2)	6 530(7)	3 203(7)	3 117(11)
O(3)	6 508(5)	4 618(5)	2 198(8)
N(3)	6 183(6)	4 546(6)	4 243(10)
C(3)	6 417(7)	4 149(8)	3 116(12)
O(4)	5 882(6)	4 526(6)	6 348(9)
C(4)	6 068(8)	4 148(8)	5 367(14)
H(1)	604(7)	304(7)	591(12)
H(3)	606(7)	506(7)	413(12)
Solvent and cationic ' oxygen ' atoms			
O(1)	0 552(12)	3 711(11)	4 793(17)
O(2)	8 413(7)	1 733(7)	6 843(11)
O(3)	6 280(7)	2 415(6)	7 867(9)
O(4)	3 564(5)	3 149(6)	8 731(10)
O(5)	8 600(16)	3 143(12)	5 506(19)
O(6)	0 157(12)	4 702(9)	7 005(14)
O(7)	7 347(6)	0 383(6)	6 880(11)
O(8)	5 081(7)	3 828(8)	8 862(13)
O(9α) †	8 104(12)	4 709(10)	6 204(20)
O(9β) †	2 056(42)	4 364(42)	6 442(68)
O(10α) †	4 476(7)	4 518(9)	1 367(13)
O(10β) †	4 483(33)	4 011(34)	2 112(55)
O(11)	7 909(19)	2 860(19)	8 615(31)

† Population parameters: α 0.8, β 0.2.

complex-ionic species in the asymmetric unit. However, it is not clear which of the remaining species refined as ' oxygen ' atoms are, in fact, the ammonium cations, the thermal motion throughout many of these atoms being very high and difference maps correspondingly inconclusive and further confused by the presence of disorder. (It has been assumed throughout that the space group is centric as suggested by the solution and intensity statistics; there is no evidence to the contrary and if the disorder is an illusory consequence of a wrong assignment of space group, the possibility of improving the model under these circumstances is remote.)

The co-ordination of these ligands to the iron atom is *fac*, each ligand being bidentate through one of the amide oxygens and the oxime nitrogen. The geometries of the $FeNOC_2$ ring fragments are similar to that found in ferroverdin[2] [also a low-spin iron(II) derivative]; in the latter mean Fe–N and Fe–O distances may be marginally shorter (1.84 and 1.95 Å) than in the present complex. These distances are consistent with the diamagnetic ground state, but the mean Fe–N distance in particular is very much shorter than that found (1.97 Å) in the diamagnetic tris(*o*-phenanthroline)-iron(II) cation.[8]

The contact O(2) · · · O(3) (2.82 Å) lies at the van der Waals distance[9] of 2.80 Å and angle O(3)–C(3)–C(2) is

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[8] A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, 1973, **12**, 1641.

[9] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

large (126.6°). Within the violurate ring system, the angles at N(1) and N(3) are considerably larger than the remainder, probably a consequence of the lack of an exocyclic conjugated bond, a fact further reflected in the size of the C(1)–C(2)–C(3) angle (121.0°) relative to N(1)–C(1)–C(2) (118.2°) in correlation with the C(2)–N(2) and C(1)–O(1) relative bond orders (Figure 2). All ligands are planar to better than 0.12 Å; the maximum deviation of the co-ordinated iron atom from any ligand is 0.15 Å.

Table 4

Interatomic distances (Å) and angles (°), least-squares estimated standard deviations in parentheses (anion metal geometries only; ligand geometries are deposited as Supplementary Publication)

	Anion (1)			Anion (2)			
Ligand	(1)	(2)	(3)	(1)	(2)	(3)	Mean
Fe–O(1)	1.974(9)	1.979(7)	1.990(6)	1.989(8)	1.992(6)	1.979(8)	1.98$_3$
Fe–N(2)	1.870(9)	1.863(7)	1.862(10)	1.893(8)	1.888(9)	1.884(9)	1.87$_7$
O(1)–Fe–N(2)	83.7(4)	84.0(3)	84.3(3)	83.3(3)	83.1(3)	84.1(4)	83.8
Fe–O(1)–C(1)	109.2(8)	109.6(6)	108.5(7)	109.0(6)	109.3(6)	109.0(8)	109.1
O(2)–N(2)–Fe	125.5(8)	126.4(6)	125.9(6)	124.1(8)	126.7(6)	126.6(7)	125.9
C(2)–N(2)–Fe	114.4(8)	114.4(6)	113.6(8)	113.2(6)	113.9(7)	112.9(8)	113.7

Other values: those for anion (2) follow those for anion (1)

Mean					Mean
89.2	O(11)–Fe–O(21)	89.4(3), 92.7(3)	O(11)–Fe–N(22)	88.5(4), 97.1(3)	92.9
	O(11)–Fe–O(31)	91.6(3), 85.1(3)	O(21)–Fe–N(32)	92.9(4), 91.7(3)	
	O(21)–Fe–O(31)	89.9(3), 87.3(3)	O(31)–Fe–N(21)	92.2(3), 95.1(4)	
94.4	N(12)–Fe–N(22)	94.8(3), 94.6(4)	O(11)–Fe–N(32)	175.2(3), 168.1(4)	172.5
	N(12)–Fe–N(32)	94.0(4), 92.7(4)	O(21)–Fe–N(12)	173.1(4), 175.2(3)	
	N(22)–Fe–N(32)	95.9(4), 94.4(4)	O(31)–Fe–N(22)	172.9(4), 170.3(3)	

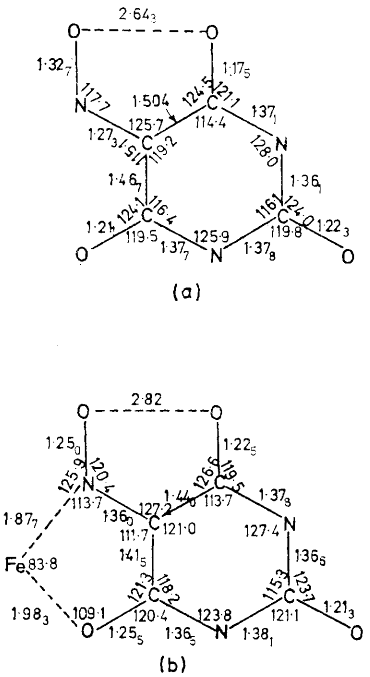
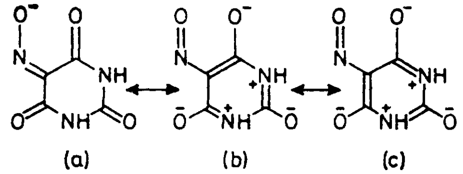


Figure 2 A comparison of mean ligand geometries within (a) the HV and (b) $[FeV_3]^-$ systems (V^- = violurate)

The ligand geometry also invites comparison with that of violurate in other derivatives studied. In copper violurate,[8,10] a similar bidentate disposition is found about the central copper atom, the Cu–N(2) bond (1.97 Å) being shorter than Cu–O(1) (2.21 Å), with a concomitant enlargement of the (Cu)ONC$_2$ ring angles. Salts of potassium, rubidium,[11,12] and strontium [13] have also been examined structurally; the geometries of the ligands are in substantial agreement with those already discussed apart from minor variations in the (M)ONC$_2$ geometries. On the other hand, appreciable and significant differences are found between the present geometry and that of perdeuteriated violuric acid monohydrate (Figure 2), most notably about the protonated nitrosyl group and its associated carbon atom.[14,15] For the violurate species a number of 'resonance forms' are possible based on the following types,



and it is apparent that in the ion and its complexes the bond lengths are such as to indicate an appreciable participation of forms based on (b) and (c). In the protonated species, however, the participation of these forms is blocked by the requirement of the single O–N bond, so that conjugation is only possible about the pair of NH groups in the ring. Thus in the acid we expect to find N(2)–O(2), C(2)–C(1), and C(2)–C(3) appreciably lengthened (as is the case). Among the possible resonance forms, that in (a) is particularly conducive to π bonding with the metal *d* orbitals and might be expected to contribute more to the bonding within the anion in metal complexes than in

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[10] M. Hamelin, *Acta Cryst.*, 1972, **B28**, 228.

[11] H. Gillier, *Bull. Soc. chim. France*, 1965, 2375.

[12] H. Gillier, *Bull. Soc. chim. France*, 1975, 2385.

[13] M. Hamelin, *Compt. rend.*, 1967, **C264**, 2034.

[14] B. M. Craven and Y. Mascerenhas, *Acta Cryst.*, 1964, **17**, 207.

[15] B. M. Craven and W. J. Takei, *Acta Cryst.*, 1964, **17**, 415 (neutron analysis).

the free ion; the accuracy of the data available for the anion and its complexes is insufficient to test this hypothesis thoroughly, and it is clear that the differences (if any) are slight. We note that co-ordination of metal ions by violurate is geometrically similar to that recently reported with the potassium salt of isonitrosoacetophenone,[16] and the ligand and co-ordination geometries are almost identical although rather more accurate. Similar analogies may be drawn with a number of other oxime structures.

The Mössbauer spectrum of each of the compounds is basically an intense sharp doublet with a very small quadrupole splitting, almost temperature independent. This doublet corresponds to the expected Mössbauer spectra for low-spin iron(II) with a small asymmetric bonding to the ligands.

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[16] M. A. Bush, H. Lüth, and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 740.