Low-spin Six-co-ordinate Cobalt(II) Complexes. A Solution Study of Tris(violurato)cobaltate(II) Ions†

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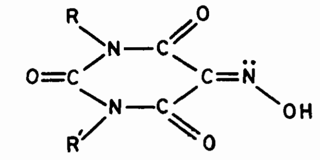
The formation of complexes of Co^{II} with violuric acid (1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime), H_3vi, and its monomethyl (H_2mvi) and dimethyl (Hdmvi) derivatives in dimethyl sulphoxide–water (80:20) has been investigated. Potentiometric, calorimetric, magnetic, and e.s.r. measurements clearly evidence that $[Co(H_2vi)_3]^-$, $[Co(Hmvi)_3]^-$, and $[Co(dmvi)_3]^-$ are low-spin octahedral complexes. The high spin–low spin change occurs upon binding of the third ligand.

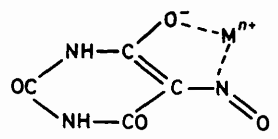
In recent years we have investigated[1] the co-ordination chemistry of violuric acid, H_3vi [1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime]. As a result, it has been shown that the anion H_2vi^- behaves as a strong-field ligand, similar to the well known 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), displaying a significant π-acceptor character. With the violurate anions cobalt(II) forms a deep green complex of 1:3 stoicheiometry. A preliminary study allowed us to suggest, despite one referee's scepticism, that $[Co(H_2vi)_3]^-$ is a low-spin octahedral complex.[2,3]

Cobalt(II) forms complexes with very diverse electronic and molecular structures. However the most usual are high-spin octahedral complexes. Very strong-field ligands are required to produce spin pairing. Ligands like phen and bipy form low-spin complexes with Fe^{2+} but not with Co^{2+}. In this way, the electronic absorption spectrum[4] and the magnetic properties[5] of $[Co(phen)_3]^{2+}$ are diagnostic of an octahedral high-spin complex. However, a recent e.s.r. study of $[Co(bipy)_3]^{2+}$ in a zeolite suggests that Δ_o should be very close to the limiting value for the spin change.[6] 2,2′:6′,2″-Terpyridine forms complexes $Co(terpy)_2X_2$ (X = Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-) that clearly exhibit a spin equilibrium.[7] The most numerous and better characterized low-spin complexes of Co^{2+} are square planar with porphyrins, Schiff bases, and related ligands. These complexes may add an axial ligand to give five-co-ordinated low-spin complexes.[8] Six-co-ordinated low-spin complexes are much more scarce.[9] The formation of a pentacyano complex, $[Co(CN)_5]^{3-}$, instead of an hexacyano complex, demonstrates the tendency of Co^{II} with strong-field ligands to give low-spin species with co-ordination numbers lower than six.[10]

The interest that low-spin cobalt(II) complexes have aroused in recent years has been reflected in the number of papers, dealing mainly with their structural features, published. However, as far as we know, no study of their formation in solution has been reported. In this paper, we present the results of a solution study of the formation of cobalt(II) complexes with H_3vi, and its monomethyl and dimethyl derivatives H_2mvi and Hdmvi. The potentiometric and calorimetric data together with the magnetic susceptibility measurements and e.s.r. spectra indicate that $[Co(H_2vi)_3]^-$, $[Co(Hmvi)_3]^-$, and $[Co(dmvi)_3]^-$ are low-spin six-co-ordinated species at room temperature. A spin change occurs when the third ligand is complexed.

There are not many examples in the literature of spin changes produced in the stepwise formation of complexes and almost everyone involves Fe^{II}. The typical examples in the textbooks are the systems iron(II)–phenanthroline and –bipyridine, although more recently some others have been reported.[3] As far as we know, no cases with Co^{II} have been described.





H_3vi R = R′ = H
H_2mvi R = Me R′ = H
Hdmvi R = R′ = Me

Experimental

Reagents.—The synthesis of the three ligands, H_3vi, H_2mvi, and Hdmvi was carried out as described elsewhere.[3,11,12] The salt $Co(NO_3)_2{\cdot}6H_2O$ and all the other chemicals were Merck reagents p.a. Dimethyl sulphoxide (dmso) was purified by distillation under reduced pressure [*ca.* 2 Torr (266 Pa)] and stored in a dark bottle over 4-Å molecular sieves. From this solvent the mixture dmso–water (80:20, w/w) was prepared. All the solutions used were prepared with this mixed solvent. Carbonate-free potassium hydroxide and perchloric acid solutions were used in the potentiometric and calorimetric measurements. All these measurements were carried out in an ionic medium of 0.1 mol dm^{-3} $KClO_4$.

Physical Techniques.—Potentiometric titrations were carried out using a reaction vessel (capacity 70 cm^3) water-thermostatted at 25.0 ± 0.1 °C; nitrogen presaturated with dmso–water (80:20) was passed over the surface of the solution. The titrant was delivered by a Crison burette-738. The potentiometric measurements were made using a Radiometer PHM 84 pH-mV meter, and a GK 2401C combined glass electrode. The titration system was controlled by an Apple IIe microcomputer

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† *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Logarithms of the proton association constants for violurate ligands at 298 K in 0.1 mol dm^{-3} $KClO_4$

Ligand	dmso–water (80:20)	Water[a]
H_2vi^-	5.71(2)[b]	4.35(1)
$Hmvi^-$	5.69(1)	4.48(1)
$dmvi^-$	5.71(3)	4.61(3)

[a] Ref. 11. [b] Values in parentheses are standard deviations in the last significant number.

equipped with a 9-in video display and one minifloppy disk driver. A Basic program[13] was used to monitor, for each titration point, the e.m.f. values and the volume of titrant added. When the observed e.m.f. was constant, within user-defined limits, the next volume of titrant was added automatically and the cycle repeated until the predefined total volume of titrant had been added. The electrode was dipped in dmso–water (80:20) for 30 min before use. Nernst's equation, $E = E^{0'} + 0.059 \log [H^+]$, was strictly obeyed by the electrode in this medium. The experimental e.m.f. values were not corrected for the liquid junction potential because this effect was negligible in the pH range investigated. The SUPERQUAD program[14] was used to process the data and calculate both the protonation and stability constants.

All calorimetric measurements were performed with a LKB batch model 10700-2 microcalorimeter. The reactions between Co^{2+} and H_2vi^- or $dmvi^-$ are fast. The heats of reaction were measured by mixing solutions of Co^{2+} and the appropriate ligand. Under the reaction conditions and employing the stability constants determined, the species and their percentages at equilibrium before and after mixing were calculated by means of the DISPOL computer program.[15] Blank experiments were carried out to correct for the enthalpy of dilution of the ligand solutions.

The *X*-band e.s.r. spectra of frozen solutions at 130 K were recorded with a Bruker ER 200D spectrometer. The magnetic susceptibility measurements were made by the Evans[16] n.m.r. method. We used the paramagnetic shift of the methyl protons of Bu^tOH added to the solutions.

Results and Discussion

Protonation Constants.—Solutions (*ca.* 2 × 10^{-3} mol dm^{-3}) of H_3vi, H_2mvi, or Hdmvi have been titrated with a KOH solution (*ca.* 2 × 10^{-2} mol dm^{-3}). The potentiometric data give curves of $\bar{j}$ *versus* $-\log [H^+]$ for the three ligands. The proton association constants have been determined using a graphical method and by computation (SUPERQUAD). In each case about 90 data points from three different experiments were used. The values obtained are shown in Table 1 together with the corresponding ones in aqueous solution.

Within experimental error, the basicity of the three ligands in dmso–water (80:20) is practically the same. At first glance, this result seems surprising (and also somewhat disappointing). As observed in aqueous solution, the inductive effect of the methyl groups should provide the following basicity trend: $dmvi^- > Hmvi^- > H_2vi^-$. However, a recent thermodynamic study on these protonation reactions in aqueous solution showed that the enthalpic and entropic contributions oppose each other, tending to minimize the differences in ΔG° and therefore in the equilibrium constants. The trend in these constants is governed by the entropy variations.[17] In dmso–water (80:20) the variations in both thermodynamic parameters should be much more similar, such that they counterbalance each other and result in the same ΔG° values for the three acids.

Table 2. Stability constants of violurato complexes of Co^{II} in dmso–water (80:20) (298 K, 0.1 mol dm^{-3} $KClO_4$)

Ligand	log β_1	log β_2	log β_3	log K_2	log K_3
H_2vi^-	4.150(2)	7.037(4)	11.257(2)	2.88	4.22
$Hmvi^-$	4.25(1)	7.31(2)	11.25(2)	3.06	3.94
$dmvi^-$	4.065(8)	7.08(2)	10.89(2)	3.01	3.81

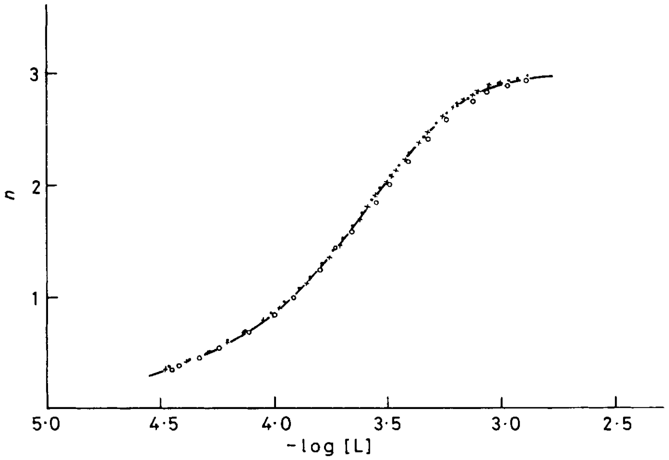

Figure 1. Formation curve for Co^{2+}–H_2vi^- complexes in dmso–water (80:20). Symbols represent experimental points. The solid line is the theoretical curve calculated with the computed constants. Formation curves for Co^{2+}–$dmvi^-$ and Co^{2+}–$Hmvi^-$ are analogous

Stability Constants of the Complexes.—Solutions of dmso–water (80:20) containing Co^{2+} and one of the violuric acids have been titrated with *ca.* 0.07 mol dm^{-3} KOH. The metal-ion concentration and the metal-to-ligand ratio were *ca.* 1 × 10^{-3} mol dm^{-3} and 1:8 respectively. The solutions of the complexes are sensitive to oxidation by atmospheric oxygen, but under our experimental conditions no oxidation to Co^{III} took place.

Potentiometric data yielded the formation curve of each system (Figure 1). The free-ligand concentration range where the complex formation occurs corresponds to a range pH* 3—6. In the calculation of the cumulative constants about 150 data points from three different experiments were used (Table 2). The distribution diagram for the species present in solution is plotted in Figure 2.

Cobalt(II) interacts with H_2vi^-, $Hmvi^-$, and $dmvi^-$ in dmso–water (80:20) to yield the stepwise formation of three complexes of 1:1, 1:2, and 1:3 stoicheiometry. However the extent of formation of the 1:2 complex is very low and it is a minor species. The predominant complex is the green $[Co(H_2vi)_3]^-$. This behaviour is very different from that observed in diluted aqueous solution where the most substituted species formed is the 1:2. This complex precipitates quantitatively from more concentrated solutions as $[Co(H_2vi)_2]\cdot 4H_2O$.[2]

The three ligands studied present almost identical behaviour. As with the protonation constants, the formation constants are also very similar. The substitution of two hydrogens by two methyl groups in the H_2vi^- anion does not improve its co-ordination ability as might initially have been thought. Conversely, $[Co(dmvi)_3]^-$ is slightly less stable than $[Co(H_2vi)_3]^-$.

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* The electrode was always calibrated as a hydrogen-ion concentration probe but, for convenience, pH instead of $-\log [H^+]$ is used through the text.

The trend in the stepwise stability constants is anomalous: $K_1 > K_2 < K_3$. Usually, the fact that $K_{n+1} > K_n$ can be attributed either to a diminution in the co-ordination number, implying a very favourable ΔS° term, or to a change in the electronic structure of the complex, characterized by a very favourable ΔH° term.[18]

As the violurato ligands are bidentate it seems reasonable to assume that these complexes are six-co-ordinated. A diminution in the co-ordination number from six to five in the third complex-formation step [equation (1)] could just occur if one of

$$[Co(H_2vi)_2(solvent)_2] + H_2vi^- \rightleftharpoons [Co(H_2vi)_3]^- + 2\ solvent \quad (1)$$

the violurate anions were unusually co-ordinated as a unidentate ligand. In this reaction, independently of the co-ordination number of the 1:3 complex, the same number of solvent molecules, two, as in the previous reaction steps are displaced. Thus, we would expect neither a particularly favourable entropic change nor an anomalous K_3 value.

It can be concluded that the trend in the stability constants strongly suggests a change in the electronic structure from a high-spin configuration, $t_{2g}^5e_g^2$, for the 1:1 and 1:2 complexes, to a low-spin configuration, $t_{2g}^6e_g^1$, for the 1:3 complexes. If this assumption is correct, the inversion in the order of the stability constants, $K_3 > K_2$, will be an enthalpy and not an entropy effect. This conclusion is fully confirmed by the calorimetric study, see below.

Microcalorimetry.—We have investigated the interaction between Co^{2+} and either H_2vi^- or $dmvi^-$ by calorimetry.

The heat evolved when mixing Co^{2+} and Hdmvi solutions in 1:8 metal-to-ligand ratio at pH between 6.9 and 7.9 has been measured. Under these experimental conditions, the free ligand $dmvi^-$ and $[Co(dmvi)_3]^-$ are the only significant species present at equilibrium, which has allowed us to determine the enthalpic change, ΔH°_t, associated with formation of the complex $[Co(dmvi)_3]^-$. In a similar way, we have determined the formation enthalpy of the complex $[Co(H_2vi)_3]^-$. In this case, the measurements were carried out at pH 6.9 since at higher pH values the evolved heat becomes pH-dependent. This dependence can surely be attributed to deprotonation of the co-ordinated H_2vi^- ligands,[1,19] a process that is obviously not possible for $dmvi^-$. On the other hand, by mixing solutions of the reagents in stoicheiometric amounts at pH 7.9, the formation enthalpy of the complex $[Co(dmvi)]^+$ has been determined. Although under these conditions the main species at equilibrium is $[Co(dmvi)]^+$ there are also significant amounts of the complex $[Co(dmvi)_3]^-$. So the experimental measurements had to be corrected for the formation of the latter species. The results obtained are shown in Table 3.

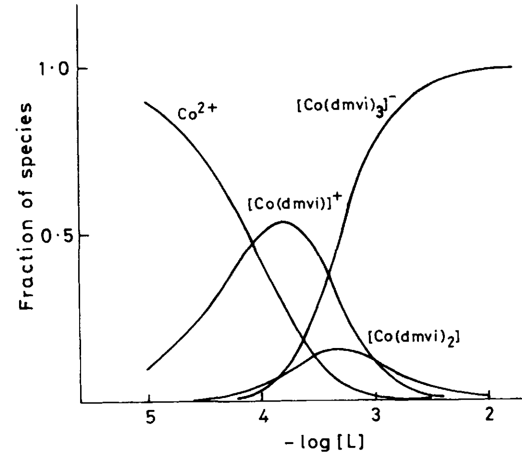

Figure 2. Distribution diagram for Co^{2+}–$dmvi^-$ complexes in dmso–water (80:20)

The stability of both 1:3 complexes is mainly due to a very favourable enthalpy. The reactions are highly exothermic, indicating a strong bonding interaction between Co^{II} and the violurato ligands. Although the entropic terms are also favourable, the enthalpic terms are by far the most important. The slightly lower stability of the complex $[Co(dmvi)_3]^-$ compared to $[Co(H_2vi)_3]^-$ can be fully attributed to its less exothermic formation. The complex $[Co(dmvi)]^+$ presents quite different thermodynamic features. Although both ΔH° and ΔS° have a favourable contribution to the stability of the complex, the entropic term is predominant. It has to be emphasized that $|\Delta H^\circ_1| < |\Delta H^\circ_t/3|$: the overall formation enthalpy is not distributed evenly between the three formation steps, it is anomalously accumulated in one of them. As $K_2 < K_1$ it seems reasonable that the enthalpic term of the second formation step, ΔH°_2, is at most as great as ΔH°_1, *i.e.* $|\Delta H^\circ_2| \leqslant |\Delta H^\circ_1|$. Accepting this, we can easily evaluate all the thermodynamic parameters associated with the stepwise formation of these Co^{II}–$dmvi^-$ complexes (see Table 4).

The formation of the 1:3 from the 1:2 complex is characterized by an anomalously high enthalpy. Co-ordination of the third ligand produces an exothermic effect six times greater than that for the first ligand. On the other hand, unlike the first step, in the third one the entropic term is unfavourable. Thus the anomalous K_3 value ($K_3 > K_2$) clearly has an enthalpic origin. The inversion in the order of the stability constants is attenuated by the entropic effects.

Our calorimetric results are in agreement with a change in the electronic structure when the third ligand is introduced. The transition of an electron from an antibonding to a bonding molecular orbital $t_{2g}^5e_g^2 \longrightarrow t_{2g}^6e_g^1$ has to be the origin of the high ΔH_3 value.

Magnetic Susceptibility Measurements.—The paramagnetic susceptibilities of a series of Co^{2+} (*ca.* 8×10^{-3} mol dm^{-3}) and

Table 3. Thermodynamic variables (kJ mol^{-1}) determined experimentally

Reaction	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$
$Co^{2+} + 3H_2vi^- \rightleftharpoons [Co(H_2vi)_3]^-$	64.10(1)	56.5(4)	7.5(4)
$Co^{2+} + 3dmvi^- \rightleftharpoons [Co(dmvi)_3]^-$	62.0(1)	52.22(8)	9.8(2)
$Co^{2+} + dmvi^- \rightleftharpoons [Co(dmvi)]^+$	23.14(4)	6.95(8)	16.2(1)

Table 4. Thermodynamic parameters (kJ mol^{-1}) for the stepwise formation of Co^{II}–$dmvi^-$ complexes in dmso–water (80:20) at 298 K and 0.1 mol dm^{-3} $KClO_4$

Reaction	log *K*	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$
$Co^{2+} + dmvi^- \rightleftharpoons [Co(dmvi)]^+$	4.06	23.14(4)	6.95(8)	16.2(1)
$[Co(dmvi)]^+ + dmvi^- \rightleftharpoons [Co(dmvi)_2]$	3.01	17.1(1)	6.95*	10.15*
$[Co(dmvi)_2] + dmvi^- \rightleftharpoons [Co(dmvi)_3]^-$	3.81	21.7(1)	38.32*	−16.62*

* Estimated value, see text.

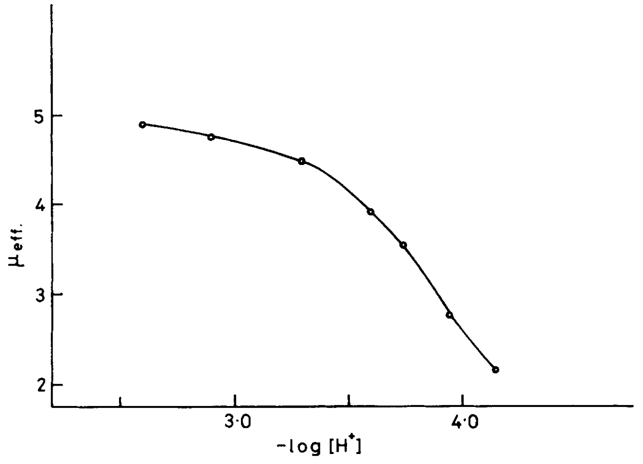

Figure 3. Effective magnetic moment of Co^{2+} as a function of pH in a Co^{2+}–H_3vi solution

violuric acid (*ca.* 4 × 10^{-2} mol dm^{-3}) solutions, varying the pH in the range 2.3—4.2, have been measured. The curve $\mu_{eff.}$ *versus* pH is plotted in Figure 3. The initial solution had a magnetic moment of 4.9 decreasing to 2.0 with increasing pH. It has not been possible to perform measurements at higher pH values because the paramagnetic shift of the indicator protons in the n.mr. spectra becomes too small ($\Delta\nu < 5$ Hz) and more concentrated solutions cannot be used due to the limited ligand solubility. However, the results are significant enough since the formation degree, $\bar{n}$, varies between 0.32 and 2.42 in the pH range studied.

It is evident that the formation of violurate complexes of Co^{II} is accompanied by an important change in the $\mu_{eff.}$ value. The initial value is characteristic of high-spin cobalt(II) complexes and reveals the existence of three unpaired electrons, while the limiting value when the 1:3 complex is fully formed should be lower than 2 indicating the presence of only one unpaired electron for each metal ion. So, the magnetic data are in accord with the thermodynamic study and show that $[Co(H_2vi)_3]^-$ is a low-spin complex at room temperature.

E.S.R. Study.—The e.s.r. spectra of a series of frozen solutions (130 K) of Co^{2+} and H_2vi^- in dmso–water (80:20) at constant metal-ion concentration but varying ratio, $x = [H_2vi^-]/[Co^{2+}]$, have been recorded. For solutions in which just the metal ion and the 1:1 complex were present no signals were observed, as expected for high-spin cobalt(II) complexes. These complexes exhibit a very short spin–lattice relaxation time in all the common stereochemistries so that very low temperatures are needed to detect any signals.[9] The situation changes with the formation of the green complex $[Co(H_2vi)_3]^-$. In Figure 4 the spectrum of a solution with $x = 5$, in which all the metal ion is complexed as $[Co(H_2vi)_3]^-$, is shown. Two intense signals are observed that can readily be explained in terms of a low-spin cobalt(II) complex with axial symmetry. The spectrum is characterized by $g_\perp = 2.22$ and $g_\parallel = 2.02$, each one of the signals being split into eight peaks because of hyperfine coupling with the cobalt nucleus ($I = \frac{7}{2}$). The parameter A^{Co} can easily be measured since the signal splitting is completely uniform. The values obtained are $A_\perp^{Co} = 50.8$ and $A_\parallel^{Co} = 74.9$ G.

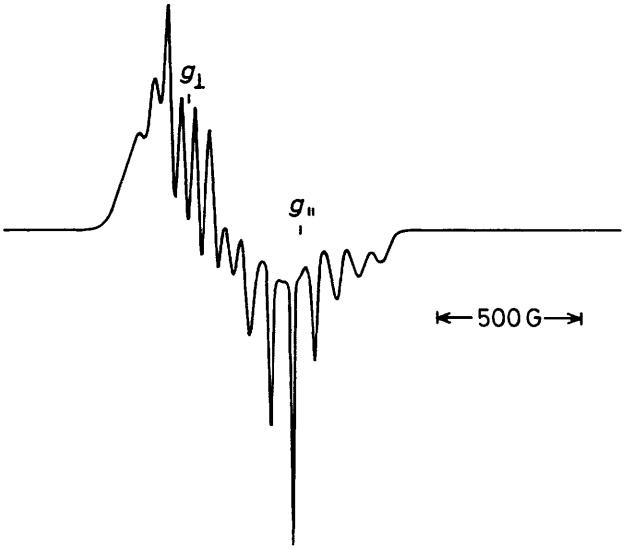

Figure 4. E.s.r. spectrum of a $[Co(H_2vi)_3]^-$ solution (*ca.* 4 × 10^{-2} mol dm^{-3}) at 130 K

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References

1 E. García-España, J. M. Moratal, and J. Faus, *Transition Met. Chem. (Weinheim, Ger.)*, 1986, **11**, 1 and refs. therein.
2 J. Faus and J. Moratal, *An. Quim.*, 1980, **76B**, 169.
3 J. Moratal, M. Julve, and J. Faus, *Rev. Chim. Miner.*, 1982, **19**, 72.
4 R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 864.
5 J. G. Schmidt, W. S. Brey, jun., and R. C. Stoufer, *Inorg. Chem.*, 1967, **6**, 268.
6 K. Misuno and J. H. Lunsford, *Inorg. Chem.*, 1983, **22**, 3484.
7 S. Kremer, W. Henke, and D. Reinen, *Inorg. Chem.*, 1982, **21**, 3013.
8 C. Daul, C. W. Schlaper, and A. von Zelewsky, *Struct. Bonding (Berlin)*, 1979, **36**, 129.
9 A. Bencini and D. Gatteschi, in 'Transition Metal Chemistry,' eds. G. A. Nelson and B. N. Figgis, Marcel Dekker, New York, 1982, vol. 8, p. 2.
10 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon, Oxford, 1984, p. 1316.
11 H. Biltz, *Chem. Ber.*, 1912, **45**, 3674.
12 H. Biltz and T. Hamburger, *Chem. Ber.*, 1916, **49**, 644.
13 M. Bartolini, A. Bianchi, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1345.
14 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
15 A. Vacca, unpublished work.
16 D. F. Evans, *J. Chem. Phys.*, 1959, 2003.
17 J. M. Moratal, A. Prades, M. Julve, and J. Faus, *Thermochim. Acta*, 1985, **89**, 343.
18 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, p. 67.
19 J. Moratal and J. Faus, *Inorg. Chim. Acta*, 1977, **25**, L1.

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