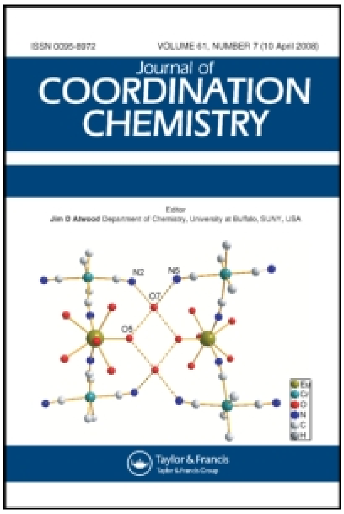

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SYNTHESIS, PROPERTIES AND STRUCTURE OF TRIS(ETHYLNITROSOLATO) COMPLEXES OF MANGANESE, IRON, AND COBALT

Pierre Gouzerh[a]; Yves Jeannin[a]; Claude Rocchiccioli-deltcheff[a]; Françoise Valentini[a]
[a] Laboratoire de Chimie des métaux de transition (Equipe de Recherche associée au C.N.R.S., n° 608), Université Pierre et Marie Curie, Paris Cedex, France

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SYNTHESIS, PROPERTIES AND STRUCTURE OF TRIS(ETHYLNITROSOLATO) COMPLEXES OF MANGANESE, IRON, AND COBALT†

PIERRE GOUZERH, YVES JEANNIN, CLAUDE ROCCHICCIOLI-DELTCHEFF and FRANÇOISE VALENTINI

Laboratoire de Chimie des métaux de transition (Equipe de Recherche associée au C.N.R.S., n° 608),
Université Pierre et Marie Curie, 4 place Jussieu, 75230 PARIS CEDEX 05, FRANCE

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A number of complexes derived from ethylnitrosolate (noted L^-) have been prepared. Complexes of general formulas ML_3 (M = Co, Fe), $M'[ML_3]$ (M = Co, Fe, Mn; M' = $N(n-C_4H_9)_4$, $P(C_6H_5)_4$ and $M''[ML_3].H_2O$ (M = Fe; M'' = Rb, Cs) have been isolated. All the complexes have been characterized by IR, visible and UV spectra measurements, magnetic susceptibility and electrochemical measurements. The voltammetric behaviour shows the existence of three members series of general type ML_3^{n-} (M = Co, Fe, Mn; n = 0, 1, 2). All the solids are low-spin. Infrared data support the assumption of the same coordination structure for all the complexes. Some assignments in the IR spectra have been proposed. The crystal structure of $Cs[FeL_3].H_2O$ has been determined by single-crystal X-ray diffraction techniques using a full-matrix anisotropic least-squares program (R = 0.081). Crystals are monoclinic in the space group $P2_1/c$ with cell parameters a = 14.97 ± 0.01 Å, b = 14.07 ± 0.01 Å, c = 14.05 ± 0.01 Å, β = 94.31 ± 0.04°. The asymmetric unit consists of two independent molecules. The ligand is bound to the iron atom via the nitrogen atom of the nitroso group and the oxygen atom of the oxime group; the complex has the facial geometry. The average Fe – N and Fe – O distances are 1.865 and 1.923 Å.

INTRODUCTION

Although the coordinating ability of amidoximes: $RC(NH_2)NOH$, hydroxyamidoximes: RC(NHOH)NOH, and nitrosolic acids: RC(NO)NOH has been recognized by Wieland,[1,2] Werner[3] and Ley[4] many years ago, only few subsequent works have been carried out on their complexes with transition metals; moreover, they have been almost limited to amidoximes.[5,6] However, recent work on nitrosolates has been concerned with some alkaline and organic salts of nitrosolic acids.[7,8,9]

Some years ago, we started a study of the coordination chemistry of ethylnitrosolic acid: $CH_3C(NO)NOH$ (noted HL) and hydroxyacetamidoxime: $CH_3C(NHOH)NOH$ (noted $H(H_2L)$). Our interest in these ligands primarily arose from their redox behaviour.[10]. Furthermore they can be considered as intermediates between hydroxamic acids and amidoximes which have a well known biological activity.[5,11,12] Nickel(II) was found quite interesting because of the formation of a particularly stable mixed complex with L^- and H_2L^-.[13,14] Iron was found to behave differently from nickel, the most stable complex being FeL_3^-.[15] This initial work has now been extended to cobalt and manganese. This paper deals with the characterization of the three ML_3^{n-} series (M = Mn, Fe, Co; n = 0, 1,2) by means of several techniques including magnetic, X-ray diffraction, IR, UV and visible absorption and electrochemical data.

EXPERIMENTAL

Preparation of the Ligands

Hydroxyacetamidoxime chlorhydrate and potassium ethylnitrosolate were respectively prepared according to the methods described by Armand.[10,16]

Preparation of the Complexes

i) cobalt complexes

– tris(ethylnitrosolato)cobalt(III): CoL_3

One ml of a 1.0 M cobalt chloride solution (1 mmol) was added under stirring to 0.504 g (4 mmol) of

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† A preliminary account of this investigation has been presented at the XVIIIth International Conference on Coordination Chemistry, Sao Paulo, Brazil (1977).

potassium ethylnitrosolate dissolved in 10 ml of water. The colour of the mixture immediately turned brown. Stirring was carried on for 15 minutes; then the addition of 1 ml of concentrated acetic acid changed the colour to brown-green and a dark solid precipitated out. It was filtered off, washed with water and air dried.

– tetrabutylammonium and tetraphenylphosphonium salts of tris(ethylnitrosolato)cobaltate(II): $[N(n\text{-}C_4H_9)_4][CoL_3]$ and $[P(C_6H_5)_4][CoL_3]$.

One ml of a 1.0 M cobalt chloride solution was added under stirring to 0.504 g (4 mmol) of potassium ethylnitrosolate dissolved in 10 ml of water. After 15 minutes, addition of tetrabutylammonium bromide or tetraphenylphosphonium chloride immediately led to a brown powder which was filtered off, washed quickly with cold water and recrystallized from methanol. Incidental filtration of the tetrabutylammonium salt after one day gave a solid which had indentical analytical data to those of the immediately filtered compound but a distinct infrared spectrum. These two forms of tetrabutylammonium tris(ethylnitrosolato)cobaltate(II) are hereafter referred to as A and B forms respectively.

ii) iron complexes

– potassium, rubidium, caesium, tetrabutylammonium and tetraphenylphosphonium tris(ethylnitrosolato)ferrate(II): $K[FeL_3]$, $Rb[FeL_3] \cdot H_2O$, $Cs[Fel_3] \cdot H_2O$, $[N(n\text{-}C_4H_9)_4][FeL_3]$, $[P(C_6H_5)_4][FeL_3]$

The preparation of the potassium salt has been previously described[15]; the other titled compounds have been obtained in a similar way: 0.630 g (5 mmol) of potassium ethylnitrosolate and 0.278 g (1 mmol) of iron (II) sulfate heptahydrate were dissolved together in 10 ml of water. The mixture was kept at room temperature for 24 hours and then filtered to remove any iron oxide. An excess of rubidium chloride, caesium chloride, tetrabutylammonium bromide or tetraphenylphosphonium chloride was then added to the filtrate. The solids were filtered off and air dried. The tetrabutylammonium and tetraphenylphosphonium salts were recrystallized from methanol.

– tris(ethylnitrosolato)iron(III): FeL_3

The preparation of FeL_3 was difficult because of the instability of this compound. Direct reaction between aqueous iron(III) and potassium ethylnitrosolate failed to give the desired compound which can be obtained by oxidation of FeL_3^-: chlorine was bubbled through a solution of 0.356 g (1 mmol) of potassium tris(ethylnitrosolato)ferrate(II) in 10 ml of water. The dark sticky solid was quickly collected, washed with water and recrystallized from ether. An alternative method involved the oxidation of FeL_3^- with ammonium cerium(IV) nitrate in 0.5 M sulfuric acid. The precipitate was treated as above.

FeL_3 is stable when perfectly dry but quickly decays when wet.

– ^{54}Fe labelled complexes

^{54}Fe was obtained from Oak Ridge National Laboratories as iron(III) oxide. The oxide was dissolved in 10 ml of 12 M hydrochloric acid, the solution evaporated almost to dryness and the residue treated with 10 ml of water. Then 0.760 g (6 mmol) of hydroxyacetamidoxime chlorhydrate were added and the pH was brought to about 5.0 by addition of sodium hydrogencarbonate. After one day the mixture was filtered to remove any precipitate; addition of caesium chloride to the filtrate led to the precipitation of $Cs[^{54}FeL_3] \cdot H_2O$. $^{54}FeL_3$ was prepared from $Cs[^{54}FeL_3] \cdot H_2O$ as described above.

iii) manganese complexes

– tetrabutylammonium tris(ethylnitrosolato)-manganate(II): $[N(n\text{-}C_4H_9)_4][MnL_3]$

First method: 0.252 g (2 mmol) of potassium ethylnitrosolate and 0.169 g (1 mmol) of manganese(II) sulfate monohydrate were dissolved together in 10 ml of water. The mixture was filtered to remove a small quantity of a not yet identified white solid. Addition of tetrabutylammonium bromide to the filtrate slowly gave a dark brown solid which was collected and recrystallized from methanol.

Second method: 1.9 g (15 mmol) of hydroxyacetamidoxime chlorhydrate were added to the solution of 0.79 g (5 mmol) of potassium permanganate in 50 ml of water. The mixture was filtered to remove a white precipitate and the preparation was carried on as above.

– tetraphenylphosphonium tris(ethylnitrosolato)manganate(II): $[P(C_6H_5)_4][MnL_3]$ was prepared in the same way as $[N(n\text{-}C_4H_9)_4][MnL_3]$.

All compounds, after air drying, were kept in *vacuo* over diphosphorus pentoxide.

Carbon, hydrogen, nitrogen and metal analyses were carried out by the Central Microanalytical Service of the C.N.R.S.

Physical Measurements

The UV and visible spectra of solutions were recorded on a Beckman DK 2 A spectrophotometer.

The IR spectra in the 4000–200 cm^{-1} range were recorded on a Beckman IR 12 spectrophotometer or a Perkin-Elmer 283 spectrophotometer, as potassium bromide or caesium iodide pellets. Far IR spectra (350–50 cm^{-1}) were obtained with a Grubb-Parsons Cube MK II interferometer as caesium iodide or polyethylene pellets.

Magnetic susceptibilities of solids were measured by the Faraday method by using a Cahn RG electrobalance calibrated with Mohr's salt. The measurements were carried out at room temperature (293 ± 1 K) and at 77 K under nitrogen.

Thermogravimetry was carried out on a Cahn RG electrobalance.

Polarograms and cyclic voltammograms were obtained in acetonitrile with a Tacussel PRG-3 polarograph, using a carbon electrode as the working electrode, a platinum wire as the counter electrode and a silver/0.01 M silver nitrate in acetonitrile electrode as the reference electrode. Tetrabutylammonium tetrafluoborate or lithium perchlorate were used as supporting electrolytes. Some experiments were also carried out in aqueous buffers, using a saturated calomel electrode as the reference. All experiments were carried out at room temperature. Solutions were deoxygenated by bubbling argon.

X-ray Studies on $Cs[FeL_3]$. H_2O

A roughly spherical crystal of approximate radius 0.5 mm was used. Preliminary crystallographic data were obtained by the precession method, using Mo $K\alpha$ radiation. Lattice constants were determined from diffractometer alignments:

$a = 14.97 \pm 0.01$ Å
$b = 14.07 \pm 0.01$ Å
$c = 14.05 \pm 0.01$ Å
$\beta = 94.31 \pm 0.04\,°$

Systematic extinctions $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ led to $P2_1/c$ space group. The computed density of 2.10 g cm^{-3} assuming eight molecules of $Cs[FeL_3]$. H_2O per unit cell agrees with the experimental density of 2.08 g cm^{-3} measured by flotation in a mixture of methyl iodide and ethyl iodide.

Data were recorded on an automatic four-circle diffractometer using Mo $K\alpha$ radiation. Intensities were measured at room temperature with a scintillation counter and a pulse height analyser set on Mo $K\alpha$ energy in such a way that 90% of the diffracted intensity was collected. A graphite monochromator was set in front of the counter.

2756 independent reflections, including 262 zeros, with $\theta < 20.0°$ were collected, using the $\theta - 2\theta$ scan with a sweep of 1.3° at zero Bragg angle and a rate of 1.24° min^{-1}; the $K\alpha_1 - K\alpha_2$ dispersion was taken into account. Background intensity was measured during 15.8 s before and after each scan, in fixed positions. Three standard reflections 8 0 0, 0 10 0, 0 0 10, were measured every 50 reflections; no anomaly was detected. All intensities were corrected for Lorentz and polarisation effects.

For each reflection, the statistical error on observed intensity was computed as:

$$Err = [I_{obs} + CORPER + FC(BAL/TFC)^2 + (PI_{int})^2]^{1/2}$$

where I_{obs} is the observed intensity, CORPER is the counting loss, FC is the background count, BAL and TFC are the times for scan and background measurements and I_{int} is the integrated intensity:

$$I_{int} = I_{obs} + CORPER - FC\,(BAL/TFC)$$

The "ignorance factor" P was set equal to 0.03.

A reflection was taken as observed if the integrated intensity was higher than the error. For each structure factor F, a standard deviation was taken as $\sigma = ERR/2F$ for observed reflections, and $\sigma = (ERR/3)^{1/2}$ for null reflections.

Computations were performed using standard programs[17]. All calculations were carried out on the CII IRIS 80 system. Atomic parameters were refined using a full-matrix least-squares program minimizing the quantity $\Sigma w^2(|Fo| - |Fc|)^2$ where Fo and Fc are the observed and calculated structure factors put on the same scale, and w is the weight taken as $1/\sigma$. R factors are defined as:

$$R = \frac{\Sigma\,|(|Fo| - |Fc|)|}{\Sigma\,|Fo|}$$

and

$$R_w = \frac{\Sigma w^2(|Fo| - |Fc|)^2}{\Sigma w^2\,|Fo|^2}$$

188 reflections with $Fo < 1.0\sigma$ were excluded from the refinement. Atomic scattering factors for Cs^+ and Fe were corrected for anomolous dispersion[18]

Solution and Refinement of the Structure

The structure was solved by direct methods using MULTAN. The positions of the caesium and iron

TABLE I
Analytical data of complexes

Element	% carbon		% hydrogen		% nitrogen		% metal (Co, Fe or Mn)	
Compound	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
$[N(n\text{-}C_4H_9)_4][CoL_3]$ A	46.7	46.97	7.8	8.01	17.3	17.44	9.7	10.49
$[N(n\text{-}C_4H_9)_4][CoL_3]$ B	46.9	46.97	8.0	8.01	17.6	17.44	10.7	10.49
$[P(C_6H_5)_4][CoL_3]$	54.1	54.63	4.4	4.40	12.6	12.74	8.6	8.95
$[CoL_3]$	22.2	22.50	2.8	2.81	26.2	26.25	18.0	18.44
$[N(n\text{-}C_4H_9)_4][FeL_3]$	47.2	47.22	8.0	8.05	17.6	17.53	10.2	10.02
$[P(C_6H_5)_4][FeL_3]$	54.7	54.88	4.4	4.80	12.9	12.80	8.3	8.54
$Cs[FeL_3]\cdot H_2O$	15.3	15.38	2.4	2.35	18.4	17.95	12.3	11.97
$Rb[FeL_3]\cdot H_2O$	17.1	17.12	2.7	2.61	20.1	19.98	13.0	13.32
$[FeL_3]$	22.6	22.71	3.0	2.83	26.6	26.50	17.7	17.91
$[N(n\text{-}C_4H_9)_4][MnL_3]$	47.6	47.31	8.2	8.06	17.3	17.55	10.0	9.86
$[P(C_6H_5)_4][MnL_3]$	55.2	55.05	4.5	4.43	12.7	12.84	8.3	8.40

atoms and of four atoms bound to iron showed up. Refinement of these positions led to $R_w = 0.29$. A three-dimensional Fourier map revealed the 30 remaining non-hydrogen atoms. Refinement of the positional and isotropic parameters of the 42 atoms decreased R_w to 0.18. Further refinement with anisotropic thermal parameters for all atoms led to $R_w = 0.083$. Attempts to correct data for absorption did not improve significantly R. The linear absorption coefficient was 35.5 cm^{-1} and the transmission coefficient ranged from 0.34 to 0.41.

The final R factors are $R = 0.081$ and $R_w = 0.083$†. These rather poor values can be explained by the fact that the asymetric unit contains two $Cs[FeL_3]\cdot H_2O$. Thus some correlations may occur between some parameters which disturb the refinement; indeed the heavy atoms are related by a pseudo-translation of a/2 along the a axis (see below).

RESULTS AND DISCUSSION

Chemical Formulas

Satisfactory analytical data were obtained for all compounds (Table I). The water content of rubidium and caesium tris(ethylnitrosolato)ferrate(II) was determined by means of thermogravimetry. The hydrated salts lose their water at about 80° C and the anhydrous are stable up to about 180° C.

Magnetic Susceptibilities

CoL_3 and $Cs[FeL_3].H_2O$ were found diamagnetic, suggesting a low-spin d^6 octahedral configuration. Room temperature magnetic moments close to 1.8 BM were obtained for both A and B forms of $[N(n\text{-}C_4H_9)_4][CoL_3]$ and for $[P(C_6H_5)_4][CoL_3]$. A slight decrease in the effective moments was observed when lowering the temperature to about 77 K. This agrees with a low-spin d^7 octahedral configuration.[19] Magnetic moments were found equal to about 1.9 – 2.0 BM for $[N(n\text{-}C_4H_9)_4][MnL_3]$ and FeL_3; this is consistent with a low-spin d^5 octahedral configuration.[19]

The low-spin character of all tris(ethylnitrosolato) complexes suggests that ethylnitrosolate is a very strong field ligand. This is especially noteworthy for cobalt because very few six-coordinate low-spin cobalt(II) complexes have been till now reported.[20]

Molecular Structure

Chemical formulas and magnetic data strongly suggest that ML_3^{n-} are octahedral complexes, each ligand being bidentate. Furthermore, chemical and spectroscopic evidence (see below) supports the assumption of the same coordination structure for all ML_3^{n-} complexes. As ethylnitrosolate can coordinate at least in three ways, namely through two oxygen atoms, two nitrogen atoms or one oxygen and one nitrogen atom, leading respectively to the syn-syn, anti-anti or syn-anti configurations, an X-ray study was undertaken in order to know the actual structure of these complexes. The crystal structure of

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†A table of observed and calculated structure factors is available as supplementary material.

TABLE II

Atomic fractional coordinates[(a,c)] and anisotropic thermal parameters (Å^2)[(b,c)]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Anion 1									
Fe(1)	6518(1)	3128(1)	3149(1)	4.68(10)	4.65(10)	2.92(9)	−0.10(7)	0.47(7)	−1.11(7)
Ligand 1									
O(1)	5574(7)	3754(8)	3742(8)	5.1(5)	6.9(6)	5.0(5)	0.1(4)	1.0(5)	−2.9(5)
N(1)	4826(9)	3856(8)	3218(9)	5.7(7)	4.4(6)	4.4(7)	0.4(5)	2.0(6)	−1.4(5)
C(1)	4865(9)	3535(10)	2354(11)	4.6(7)	4.2(7)	5.0(8)	1.1(5)	1.6(6)	0.6(6)
N(2)	5643(7)	3099(8)	2137(7)	5.2(6)	4.4(5)	1.6(5)	−0.7(4)	0.5(4)	−0.1(4)
O(2)	5662(7)	2730(8)	1338(7)	5.9(5)	7.1(6)	2.9(5)	0.8(4)	0.4(4)	−0.3(4)
C(2)	4087(10)	3582(13)	1625(13)	4.3(7)	7.2(10)	7.3(10)	1.4(7)	0.7(7)	−1.2(8)
Ligand 2									
O(1)	7170(7)	3114(9)	4387(7)	6.3(5)	7.7(7)	2.1(4)	−1.1(5)	−0.1(4)	−2.0(5)
N(1)	7114(9)	2299(12)	4864(8)	6.2(7)	8.4(9)	1.9(5)	0.4(6)	0.0(5)	−0.5(6)
C(1)	6640(9)	1648(11)	4426(9)	4.8(6)	6.3(8)	1.9(6)	0.0(6)	0.3(5)	−0.6(6)
N(2)	6284(7)	1887(8)	3507(7)	5.0(5)	5.1(6)	2.3(5)	0.6(5)	−0.6(4)	−1.8(5)
O(2)	5883(7)	1236(7)	3052(7)	7.3(6)	4.9(5)	3.7(5)	−0.2(5)	0.4(4)	−0.5(4)
C(2)	6456(13)	699(12)	4854(11)	9.8(11)	5.8(9)	3.2(7)	1.1(8)	0.4(7)	1.3(6)
Ligand 3									
O(1)	7014(8)	4386(8)	2983(9)	6.9(6)	5.5(6)	7.2(7)	−0.3(5)	1.1(5)	−2.4(5)
N(1)	7716(9)	4423(10)	2481(10)	6.5(7)	5.7(8)	5.1(7)	−1.0(6)	−0.1(6)	−1.5(6)
C(1)	7945(9)	3601(11)	2162(9)	5.2(7)	4.5(8)	2.9(6)	−1.8(6)	−1.2(5)	0.3(6)
N(2)	7438(7)	2818(9)	2392(7)	5.8(6)	4.0(6)	1.4(4)	1.2(5)	−0.1(4)	−1.1(4)
O(2)	7611(6)	2025(8)	2060(6)	5.8(5)	5.6(6)	2.3(4)	0.8(4)	0.2(3)	0.2(4)
C(2)	8741(10)	3482(13)	1559(11)	4.8(7)	9.1(11)	4.2(7)	-1.3(7)	2.5(6)	−0.3(7)
Anion 2									
Fe(2)	1525(1)	3286(1)	3052(1)	4.70(10)	4.25(9)	2.47(9)	0.31(7)	−0.16(7)	−0.66(7)
Ligand 1									
O(1)	2071(7)	4485(7)	2793(7)	7.1(6)	5.1(5)	3.8(6)	−0.6(4)	−1.0(4)	−1.6(4)
N(1)	1989(9)	4776(8)	1884(9)	6.3(6)	4.7(6)	3.4(6)	−0.1(5)	−0.9(5)	0.2(5)
C(1)	1534(10)	4190(10)	1337(11)	5.8(7)	3.2(6)	4.7(8)	−0.4(6)	0.3(6)	−0.1(6)
N(2)	1197(7)	3379(9)	1736(7)	4.0(5)	5.2(6)	2.2(5)	0.6(5)	−0.8(4)	−0.7(5)
O(2)	789(7)	2795(7)	1211(7)	6.3(5)	5.2(5)	3.5(4)	−0.6(4)	−1.2(4)	−0.7(4)
C(2)	1376(13)	4335(14)	266(11)	8.7(10)	8.9(10)	3.2(8)	0.4(9)	−0.9(7)	1.7(7)
Ligand 2									
O(1)	580(8)	4007(8)	3561(7)	6.9(6)	5.5(5)	3.9(5)	1.8(5)	−0.3(4)	−2.0(4)
N(1)	−117(8)	3500(13)	3781(9)	3.2(6)	9.0(10)	4.5(6)	1.0(6)	0.3(4)	−0.5(6)
C(1)	−51(10)	2578(12)	3671(9)	5.3(8)	5.8(9)	2.0(6)	0.9(7)	0.2(5)	0.1(6)
N(2)	718(7)	2297(8)	3249(7)	5.0(6)	3.3(6)	2.1(4)	0.3(4)	0.7(4)	0.1(4)
O(2)	765(7)	1449(8)	3044(7)	6.6(6)	4.9(6)	4.6(5)	−0.4(4)	1.4(4)	0.1(4)
C(2)	−762(11)	1929(15)	3879(13)	4.7(8)	10.3(12)	5.7(9)	−0.1(8)	0.9(6)	1.8(8)
Ligand 3									
O(1)	2149(7)	3357(8)	4287(6)	5.9(5)	7.6(6)	2.1(4)	1.0(5)	−1.1(3)	−0.5(4)
N(1)	2854(8)	2806(10)	4429(7)	5.2(6)	7.4(7)	1.8(5)	0.2(6)	−0.7(4)	−0.1(5)
C(1)	3026(9)	2277(11)	3688(11)	3.6(6)	6.1(8)	3.9(7)	−0.2(4)	−0.9(6)	1.1(7)
N(2)	2437(7)	2419(7)	2862(8)	4.6(5)	3.5(5)	3.4(6)	−0.2(4)	0.5(4)	−0.7(5)
O(2)	2552(7)	1912(8)	2160(7)	6.6(5)	5.5(5)	3.9(5)	0.9(4)	0.5(4)	−1.1(4)
C(2)	3781(11)	1593(14)	3672(13)	5.1(8)	7.9(10	6.7(10)	1.8(7)	−0.7(7)	1.2(8)
Cations									
Cs(1)	62307(6)	5980(6)	9183(5)	6.83(6)	4.47(6)	2.19(5)	−0.90(4)	0.24(3)	0.04(3)
Cs(2)	10902(7)	6146(7)	9376(6)	8.34(7)	4.53(6)	2.47(5)	−0.72(4)	−0.41(4)	0.09(3)
Solvent molecules									
E(1)	3989(9)	860(9)	836(8)	9.2(7)	6.3(6)	5.1(6)	1.0(5)	0.5(5)	−1.5(4)
E(2)	−1166(11)	903(10)	773(10)	11.3(9)	7.1(7)	8.0(8)	2.1(6)	3.2(7)	−0.1(6)

(a) Atomic fractional coordinates x 10^4 (x 10^5 for the two Cs^+)

(b) Anisotropic thermal parameters in the form:

$$\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$$

(c) Estimated standard deviations in the final digit are given in parentheses

$Cs[FeL_3] . H_2O$ has been investigated first because this compound easily gives nice single crystals.

The asymmetric unit is made of two independent molecules. The caesium atoms, the water molecules, the iron atoms and their immediate surroundings are roughly related by a pseudo-translation of a/2 along the a axis; but the two whole complex anions are eniantomers.

The atomic parameters with their standard deviations are given in Table II. Atomic numbering within the ligand is shown in Figure 1. Figure 2 shows a projection of the asymmetric unit down the b axis.

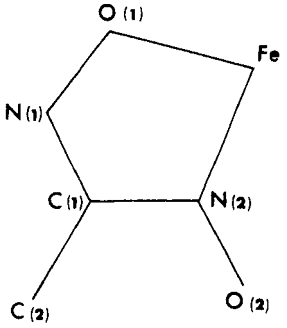

FIGURE 1 Atomic numbering within the ligand.

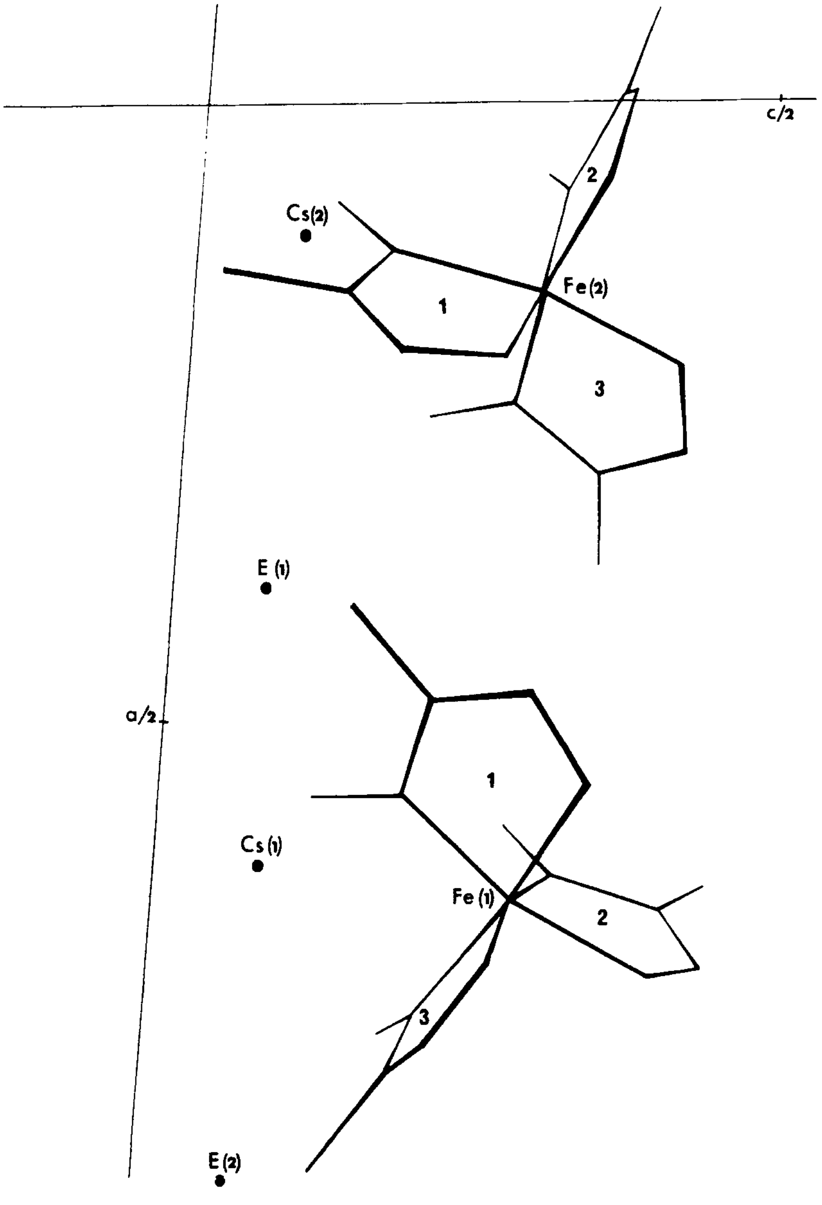

FIGURE 2 Perspective view of the asymmetric unit down the b axis.

TABLE III

Interatomic distances (Å) and angles (°), estimated standard deviations in parentheses

	Anion 1			Anion 2			
Ligand	1	2	3	1	2	3	mean
Fe-O(1)	1.909(10)	1.929(9)	1.939(12)	1.921(11)	1.922(10)	1.910(9)	1.923(10)
Fe-N(2)	1.859(11)	1.858(13)	1.853(11)	1.881(10)	1.876(11)	1.864(11)	1.865(11)
N(1)-O(1)	1.300(16)	1.333(17)	1.310(18)	1.337(15)	1.320(17)	1.313(15)	1.319(16)
N(2)-O(2)	1.240(14)	1.245(14)	1.244(14)	1.235(14)	1.230(14)	1.239(14)	1.239(14)
C(1)-N(1)	1.300(19)	1.287(19)	1.295(19)	1.285(18)	1.311(20)	1.321(19)	1.300(19)
C(1)-N(2)	1.370(17)	1.399(18)	1.389(18)	1.384(18)	1.390(18)	1.418(17)	1.392(18)
C(1)-C(2)	1.492(23)	1.498(23)	1.522(21)	1.518(23)	1.448(24)	1.485(23)	1.494(23)
O(1)-Fe-N(2)	80.9(5)	80.7(5)	80.7(5)	80.6(5)	80.6(5)	81.5(5)	80.8(5)
Fe-O(1)-N(1)	115.9(8)	114.6(8)	115.5(9)	116.0(8)	114.8(9)	116.1(7)	115.5(8)
O(1)-N(1)-C(1)	113.2(11)	115.1(11)	113.2(12)	112.5(12)	116.0(12)	114.5(10)	114.1(11)
N(1)-C(1)-C(2)	122.6(13)	123.5(13)	121.9(14)	122.9(14)	122.4(15)	124.8(13)	123.0(14)
N(1)-C(1)-N(2)	117.4(13)	115.4(13)	117.6(13)	118.6(13)	113.8(13)	114.8(12)	116.3(13)
C(2)-C(1)-N(2)	119.9(13)	121.1(14)	120.4(14)	118.5(14)	123.4(15)	120.4(14)	120.6(14)
C(1)-N(2)-Fe	112.5(9)	114.2(9)	112.9(10)	112.3(9)	114.5(10)	113.1(9)	113.3(9)
C(1)-N(2)-O(2)	117.8(11)	115.6(12)	119.3(11)	119.0(11)	116.0(11)	117.0(11)	117.4(11)
Fe-N(2)-O(2)	129.7(9)	130.2(8)	127.7(9)	128.5(9)	129.5(8)	129.6(9)	129.2(9)

Table III lists intramolecular bond distances and bond angles with their standard deviations.

Each ligand is bound to the iron *via* the nitrogen atom N(2) of the nitroso group and the oxygen atom O(1) of the oxime group; the complex has the facial geometry. It is worth pointing out that the ligand exhibits the same syn-anti configuration as in (ethylnitrosolato)(hydroxyacetamidoximato)-nickel(II).[14] It is also of some interest that other Fe(II) octahedral complexes of ligands which can be expected to coordinate *via* the nitrogen atom of a nitroso group and an oxygen, forming a five-membered ring, have also the facial geometry.[21,22] However, the origin of the predominance of the facial geometry is not known.[23]

The mean Fe-N and Fe-O distances are consistent with those found in Fe(II) octahedral complexes having a diamagnetic ground state.[21,22] Furthermore, the geometry of the ligand is quite similar to that previously found in the nickel complex;[14] again the C – N and N – O distances show significant localization along the ONCNO chain.

TABLE V

Equations of least-squares mean planes through chelate rings, in the form Ax + By + Cz – D = O, and deviations of the defining atoms from the planes, in Å.

	Anion 1			Anion 2		
Chelate ring	1	2	3	1	2	3
A	5.2508	12.955	8.3114	12.909	5.4952	9.0446
B	12.317	–4.3389	–2.2149	–6.6636	–2.0735	10.234
C	–5.0199	–6.4404	10.852	–3.4053	12.476	–5.1879
D	5.6939	5.0613	8.1407	–1.2604	3.9636	3.1590
Fe	0.001(2)	–0.002(2)	0.001(2)	0.001(2)	0.001(2)	–0.001(2)
O(1)	–0.022(11)	0.050(10)	–0.045(12)	–0.005(11)	–0.032(10)	–0.004(11)
N(1)	–0.026(12)	0.024(12)	–0.014(13)	0.005(13)	–0.036(12)	–0.004(12)
C(1)	0.034(14)	–0.024(13)	0.010(13)	–0.006(14)	0.053(12)	–0.005(14)
N(2)	0.014(10)	0.003(10)	0.013(10)	–0.037(10)	0.008(9)	0.037(10)
O(2)	–0.031(11)	0.059(10)	–0.027(8)	0.004(10)	–0.046(10)	–0.014(11)
C(2)	0.048(18)	–0.125(19)	0.046(15)	0.057(20)	0.058(17)	–0.014(19)
Average deviation	0.025	0.041	0.022	0.016	0.034	0.011

The ligand is nearly planar within experimental errors. The equations of least-squares mean planes through chelate rings, in the form $Ax + By + Cz - D = 0$, and the deviations of the defining atoms from the planes (in Å) are given in table V.

The shortest distance between a water molecule and an oxygen of the complex anion is 2.94(2) Å; thus hydrogen bonds, if any, are necessarily weak. This is consistent with the easy dehydration of the compound.

Infrared Spectra

The IR spectra of the complexes are shown in Figure 3 and 4. Although the spectra are different, they present sufficient analogous features to allow the assumption of the same coordination for all the ML_3^{n-} (n = 0, 1) compounds, namely that reported above for $Cs[FeL_3] \cdot H_2O$.

The IR spectra of nickel(II) complexes with ethylnitrosolic acid and/or hydroxyacetamidoxime have been previously reported.[24] The IR spectrum of CoL_3 is quite similar in the high-frequency region (1600–700 cm^{-1}) to that of NiL_2. It seems then reasonable to relate the band pattern between 1550 and 1350 cm^{-1} to the asymmetric stretching vibrations $\nu_{as}NCN$ (with some δCH_3 character), and the strong bands at 1220 cm^{-1} and at about 1100–1150 cm^{-1} to the ν N – O stretching

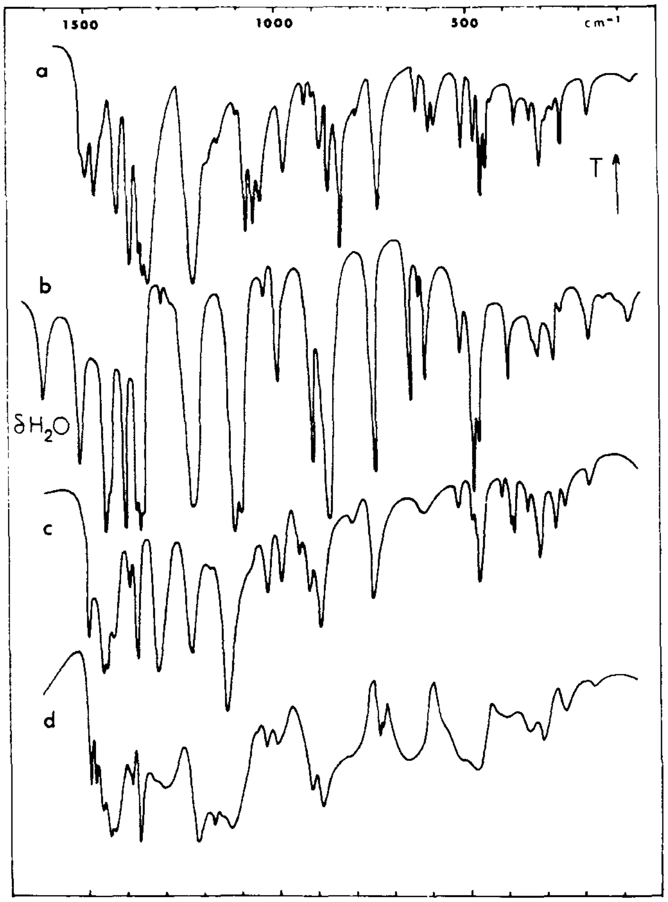

FIGURE 3 Infrared spectra of ML_3^- complexes:
a $[N(n-C_4H_9)_4][MnL_3]$
b $Cs[FeL_3] \cdot H_2O$
c $[N(n-C_4H_9)_4][CoL_3]$ (A form)
d $[N(n-C_4H_9)_4][CoL_3]$ (B form)

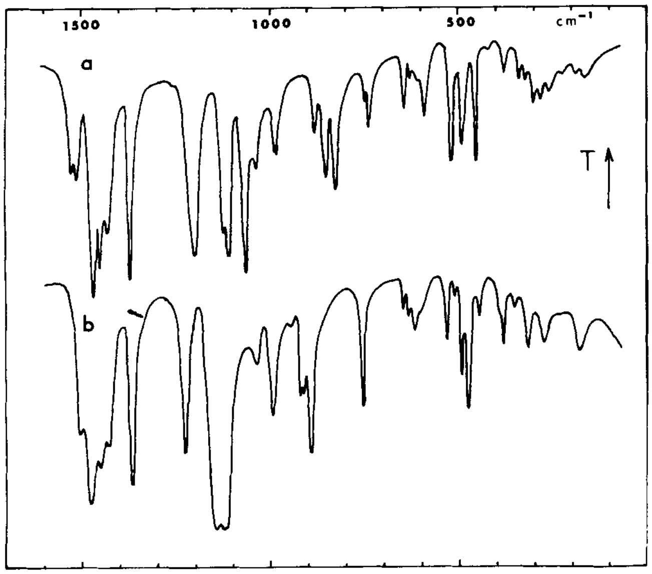

FIGURE 4 Infrared spectra of ML_3 complexes
a FeL_3
b CoL_3

vibrations corresponding respectively to the short and long N – O bonds. Similar assignments can be made in the spectrum of FeL_3.

In addition to these ν_{as}NCN and νN – O stretching vibrations, the IR spectra of ML_3^- compounds show another strong absorption between 1360 and 1300 cm^{-1} (Figure 3 a, b, c), which seems characteristic of these charged complexes. Thus the ML_3^{n-} complexes are to be classified into two groups, the ML_3 group (M formal oxidation state: III) and the ML_3^- group (M formal oxidation state: II). Similarly, Saito *et al.*[25] have reported that the spectra of the tris(2,2′-bipyridine) complexes of Fe(II) and Fe(III) are as well different in the high frequency region. On the contrary, the IR spectra are similar in the low-frequency region when changing the formal oxidation state from M(II) to M(III). Moreover, in this region, the spectra of all the complexes do not change appreciably with the metal.

It is worth comparing these results with those obtained by several authors[25,26,27] on a series of octahedral complexes involving 2,2′-bipyridine, 1,10-phenanthroline and thiocyanate ligands

TABLE IV
νM – N and/or νM – O stretching frequencies of some octahedral metal complexes

	d^5		d^6		d^7		
complexes	Mn^{II}	Fe^{III}	Fe^{II}	Co^{III}	Co^{II}	Ref.	Assignments
$[M(bipy)_3]^{n+}$ n = 2,3	{224 191 h.s.	{384 367 l.s.	{381 374 l.s.		{266 228 h.s.	(25)	νM – N
$[M(phen)_3]^{n+}$		{374 354 l.s	{374 359 l.s.	{378 370 l.s.		(25)	νM – N
$[M(bipy)_2(NCS)_2]$			{393 374 l.s.			(26)	νM – N (bipy)
			{253 235 h.s.			(26)	νM – N (bipy)
$[M(phen)_2(NCS)_2]$			{379 371 l.s.			(26)(27)	νM – N (phen)
			{252 220 h.s.			(26)(27)	νM – N (phen)
$[M(tripyam)_2]^{2+}$			307 l.s.		{312 301 l.s.	(28)(29)	νM – N
					263 h.s.	(28)(29)	νM – N
$[M(acac)_3]$		298 h.s.		385 l.s.		(30)	νM – O
$[M(tropolonate)_3]$		{312 255 h.s.				(31)	νM – O
$[ML_3]^{n-}$ n = 0,1	{378 338 l.s.	{378(3)* 338(3)* l.s.	{404(2)* 396(3)* 328(5)* l.s.	{380 352 l.s.	{385 378 342 l.s.	this work	νM – N + νM – O

*^{54}Fe – ^{56}Fe induced shifts
l.s.: low spin; h.s.: high spin

bipy: 2,2′-bipyridine
acac: acetylacetonate

phen: 1,10-phenanthroline
tripyam: tri-(2-pyridyl) amine

(Table IV). All the low-spin complexes present M – N stretching vibrations at much higher frequencies than high-spin complexes, as reported in Table IV. Moreover, the M – N stretching frequencies do not depend on the oxidation state, unless there is a crossover in electron configuration. Saito *et al.*[25] explain the similarity of M – N stretching frequencies in low-spin complexes by a more considerable interaction between the metal d_π orbitals and the antibonding ligand π^* orbitals as the formal oxidation state is lowered.

We have already pointed out that all the ML_3^{n-} complexes are spin-paired. Therefore, since the magnetic state is the most important feature when assigning the metal-ligand vibrations, we have compared the IR spectra with those of other low-spin octahedral complexes with metal-nitrogen and metal-oxygen bonds. As it can be seen in Table IV, the M – N stretching modes are generally observed between 350 and 390 cm^{-1}, except for the low-spin iron(II) and cobalt(II) complexes of tri-(2-pyridyl)amine,[28,29] and the M – O stretching mode at 385 cm^{-1} [30]. The M – O stretching vibrations of high-spin complexes[30,31] reported in Table IV are at lower frequencies (~250–300 cm^{-1}) than those of low-spin complexes, exactly as for complexes involving M – N bonds.

In the ML_3^{n-} complexes, the idealized MN_3O_3 octahedra have the C_3 symmetry. Thus two νM – N and two νM – O stretching, of the A type and of the E type, are expected. From the results reported above, these vibrations are expected in the same frequency region (350–390 cm^{-1}).

From these considerations, the two (or three) bands observed in this region (Table IV) are assigned to vibrations with a mixed character of M – N and M – O stretching.

These assignments have been confirmed by using the metal isotope technique: the ^{56}Fe – ^{54}Fe induced shifts are indicated in Table IV for both Fe(II) and Fe(III) complexes. Other bands at lower frequencies are slightly metal sensitive and can be related to bending modes of the FeN_3O_3 octahedron and of the chelate rings.

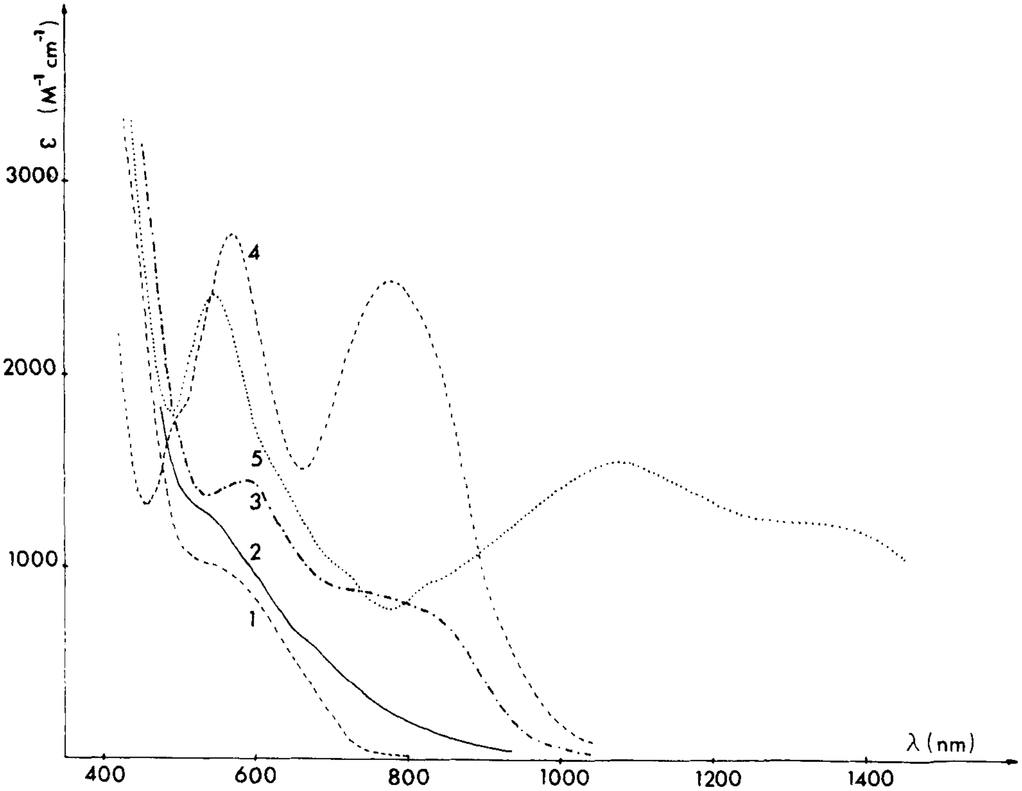

FIGURE 5 Visible absorption spectra of CoL_3 (1), $[N(n-C_4H_9)_4][CoL_3]$ (2), FeL_3 (3), $[N(n-C_4H_9)_4][FeL_3]$ (4) and $[N(n-C_4H_9)_4][MnL_3]$ (5) in CH_3CN.

Electronic Spectra

All the nitrosolato complexes reported here are deeply coloured; solids look black. The electronic spectra of acetonitrile solutions are shown in Figures 5 and 6. It must be pointed out that both A and B forms of $[N(n\text{-}C_4H_9)_4][CoL_3]$ give identical spectra.

A common feature of all the spectra is the occurrence of a very intense absorption band near 300 nm. Such a band is also present in the spectrum of the free ligand and has been assigned to a $\pi \rightarrow \pi^*$ transition.[10] This band is shifted towards greater energy in complexes; a similar shift is observed when the free ligand is protonated; therefore, this shift is assumed to show the loss – at least partial- of π delocalization which occurs under complexation or protonation.

The interpretation of the visible part of the spectra is not so simple. The visible spectrum of free ethylnitrosolate exhibits two absorption bands at 505 and 650 nm: they have been respectively assigned to $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions.[8] It can be seen that all the spectra have at least one band between 500 and 600 nm, which might be related to the $n \rightarrow \sigma^*$ transition. However, the intensity of this band and of the others is by far greater than for the free ligand. Thus these bands may have some charge transfer character.

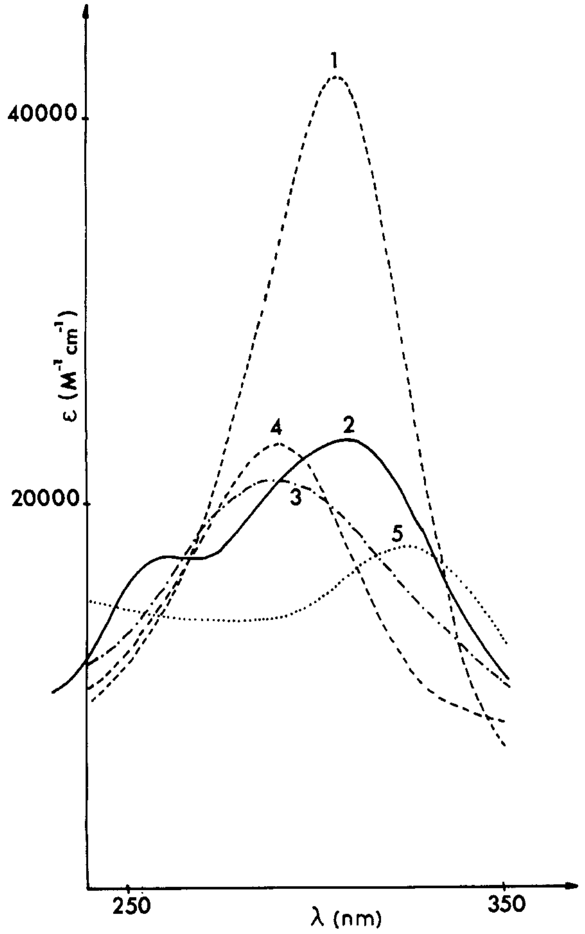

FIGURE 6 UV absorption spectra of CoL_3 (1), $[N(n-C_4H_9)_4][CoL_3]$ (2), FeL_3 (3), $[N(n-C_4H_9)_4][FeL_3]$ (4) and $[N(n-C_4H_9)_4][MnL_3]$ (5) in CH_3CN.

MnL_3^- differ from the other reported complexes by showing strong absorption in the near IR region.

Electrochemical Behaviour

Voltammogramms of ML_3^- complexes at the rotating carbon electrode (rce) show that they undergo both oxidation and reduction in acetonitrile (Figure 7). Comparison with the polarograms of FeL_3 and CoL_3 clearly shows that the anodic wave of ML_3^- arises from its oxidation to ML_3. Cyclic voltammograms indicate that the process is not strictly reversible, the separation between the cathodic and anodic peaks being always larger than the theoretical value of 59 mV for a one-electron transfer; moreover this separation increases with the scan rate.

In contrast to anodic waves, cathodic waves of the ML_3^- species are rather poorly defined in acetonitrile and, furthermore, markedly dependent upon the nature of the supporting electrolyte. For example, FeL_3^- gives a cathodic wave in the presence of lithium perchlorate but not in the presence of tetrabutylammonium tetrafluoborate. However, well defined reduction waves were obtained for the three complexes, both at the rotating carbon electrode and at the dropping mercury electrode, in aqueous alkaline buffers. Comparison of the height of the cathodic waves with that one of the anodic waves, in acetonitrile, as well as coulometric experiments, in aqueous buffers, have established that the cathodic waves also correspond to one-electron transfers. Again, cyclic voltammetry shows that the cathodic process is not strictly reversible. So far salts of ML_3^{2-} have not been isolated, but the complex anions occur in solution.

These results clearly lead to a series of three members linked by one-electron transfers:

$$ML_3 + e^- \rightleftharpoons ML_3^- + e^- \rightleftharpoons ML_3^{2-} \quad (M = Mn, Fe, Co)$$

The most striking difference between these three metals lies in the accessibility to ML_3. Whereas CoL_3^- is easily oxidized to CoL_3 (ethylnitrosolic acid itself can oxidize CoL_3^- to CoL_3 in weakly acid medium),

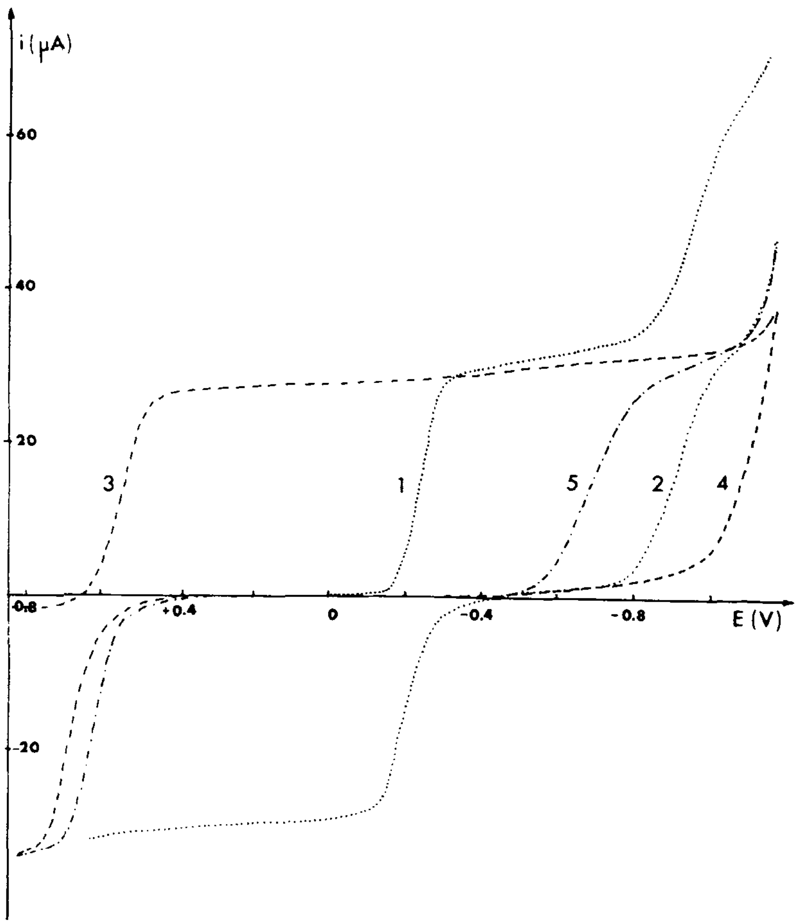

FIGURE 7 Voltammograms of CoL_3 (1), $[N(n-C_4H_9)_4][CoL_3]$ (2), FeL_3 (3), $[N(n-C_4H_9)_4][FeL_3]$ (4) and $[N(n-C_4H_9)_4][MnL_3]$ (5) at the rce, in CH_3CN and 0.1 M tetrabutylammonium tetrafluoborate. Potentials refer to the Ag/0.01 M $AgNO_3$ in CH_3CN reference electrode.

very powerful oxidizing reagents are needed for the oxidation of FeL_3^- and MnL_3^-. All the attempts to get MnL_3 by chemical or electrochemical oxidation of MnL_3^- have always resulted in the decomposition of MnL_3^-. FeL_3 is less unstable than MnL_3 and can be isolated (see experimental). However it is rather quickly reduced to FeL_3^- in solution, possibly through internal redox reaction between the central metal atom and the ligand.

It must be added that ML_3^{2-} only represents the first reduction step of ML_3^- which can fix up to six electrons, together with some protons, in aqueous solution. Indeed the ligand itself can also be reduced, leading to hydroxyacetamidoxime.[10]

CONCLUSION

The reactions of manganese, iron and cobalt with ethylnitrosolate are quite similar. In each case, the occurrence of ML_3^{n-} complexes (n = 0, 1,2) has been established and several complexes have been isolated. Chemical and spectroscopic studies show that all the complexes have the same coordination structure, i.e. a facial geometry with the three ligands bound to metal by one nitrogen and one oxygen in a syn-anti configuration.

The ligand field of ethylnitrosolate is strong enough to always give low-spin ML_3^{n-} complexes at room temperature. In ML_3 and ML_3^- the metal oxidation states can be reasonably assumed as III and II respectively. This assumption is supported by IR data. Furthermore the chemical behaviour is in agreement with the general knowledge of manganese, iron and cobalt in their oxidation states III and II. The oxidation state is less obvious for the ML$_3^{2-}$ complexes. Taking into account the easy reduction of the ligand, it may be questioned whether they are better considered as M(I) complexes with ethylnitrosolate or as M(II) complexes with reduced ethylnitrosolate. The ML$_3^{2-}$ complexes possibly have delocalized ground state although the electronic spectra show no sharp discontinuity between ML$_3^-$ and ML$_3^{2-}$.

ACKNOWLEDGEMENTS

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