impurity bands at 1172 and 630 cm^{-1} (not reported in Table II) were varied by repeated recrystallizations, as would be expected if a band of $[Co(NH_3)_6]Cl_2$ were partially obscuring a real band. These assignments do seem reasonable and when compared to previous work on the nitrosylruthenium complexes definitely indicate the isomer to be monomeric.

From the location of the NO stretching frequency, it seems appropriate to assign a negative charge to this group. A comparison of the NO stretch at 1610 cm^{-1} in this compound to the range observed in the ruthenium nitrosyls (1830–1900 cm^{-1}) shows the great weakening of the N–O bond. This is most easily interpreted in terms of the change in bond order expected when the charge on the group is changed from -1 to $+1$. During decomposition the NO^- in acid solution reduces the Co(III) to Co(II), explaining the observed decomposition products. The only other case where an NO^- ligand is believed to be present in a monomeric ion is in $K_3[Co(NO)CN)_5]$[8,9] and the complexes prepared by Feltham and Nyholm.[12] All of the ammine frequencies in the complex were located at normal frequencies. However, one might note the large splitting of the Co–NH_3 stretching frequency perhaps due to some *trans* bond weakening effect as we observed earlier in the ruthenium nitrosyl complexes.[18]

Our assignment for the NO stretching frequency for the "red" isomer is in disagreement with the assignments of Griffith, *et al.*[8,9] The observed shifts with ^{15}NO substitution compare so favorably with the calculated values for the three peaks found between 900 and 1200 cm^{-1} that there can be little question of the presence of a nitrogen–nitrogen bond in these isomers. Undoubtedly, the idealized descriptions of the normal modes are only rough approximations and a considerable amount of mixing is present. The interpretation of the spectrum below 700 cm^{-1} is considerably more speculative. The isotopic shifts do indicate the presence of at least one Co–NO bond. The final decomposition products and chemical analyses also strongly support a hyponitrite-bridged dimer.

While the infrared activity of the N–N stretching vibration would be consistent with a *cis*-hyponitrite in which the cobalt atoms are bonded to the nitrogen atoms, steric requirements seem almost certainly to prohibit this configuration. However, this *cis* configuration in which the cobalt is bonded to the oxygen atoms is entirely possible. On the other hand, the related *trans*-hyponitrite seems inconsistent with the infrared activity of the 1136-cm^{-1} band. However, the activity of this band could arise from a lowering of the site symmetry by the crystal lattice. A third alternative that has not been previously considered is an unsymmetrical structure in which one cobalt atom is bonded to the oxygen atom of the hyponitrite and the other to a nitrogen atom. While such a structure is quite uncommon, it is most consistent with our experimental data.

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Five-Coordinated High-Spin Complexes of Cobalt(II) and Nickel(II) with Bis(2-dimethylaminoethyl) Sulfide

By M. CIAMPOLINI and J. GELSOMINI

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The tridentate ligand bis(2-dimethylaminoethyl) sulfide (Me_4daes) forms 1:1 complexes with the chlorides, bromides, and thiocyanates of cobalt(II) and nickel(II). These complexes have been studied with spectral, conductivity, and molecular weight measurements. The complexes are five-coordinated in the solid state while in solution at room temperature they give rise to an equilibrium between monomeric five-coordinated and associated species. Tetrahedral species are also present at elevated temperatures.

Introduction

In this laboratory systematic research is in progress to determine the preparative conditions and characteristics of high-spin five-coordinated complexes of the metals of the first transition group.[1–4] With regard to the influence of donor atoms on the magnetic properties of five-coordinated compounds, it would appear that oxygen and nitrogen lead to a high-spin configuration, in contrast to phosphorus and arsenic which lead to a low-spin configuration. The behavior of sulfur is however uncertain because in the known

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(1) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965); *J. Am. Chem. Soc.*, **87**, 3102 (1965).

(2) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

(3) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).

(4) M. Ciampolini and N. Nardi, *ibid.*, **6**, 445 (1967).

TABLE I

PROPERTIES AND ANALYSIS OF THE M(II) COMPLEXES

Compd	Molar conductance,[c] cm² ohm⁻¹ mole⁻¹	M(found)/M(calcd)[d]	% N		% metal		% halogen	
			Calcd	Found	Calcd	Found	Calcd	Found
Co(Me$_4$daes)Cl$_2$	0.04	1.17	9.15	9.26			23.16	23.24
Co(Me$_4$daes)Br$_2$	0.04	1.17	7.10	7.20			40.45	40.58
Co(Me$_4$daes)(NCS)$_2$	0.05	1.17	15.94	15.92	16.77	16.70		
Ni(Me$_4$daes)Cl$_2$[a]	0.04	1.27	9.16	9.20	19.18	18.98	23.18	23.14
Ni(Me$_4$daes)Br$_2$[b]	0.02	1.21	7.09	7.04			40.48	40.17
Ni(Me$_4$daes)(NCS)$_2$	0.01	1.26	15.96	15.80	16.71	16.55		

[a] *Anal.* Calcd: S, 10.48. Found: S, 10.21. [b] *Anal.* Calcd: C, 24.34; H, 5.11. Found: C, 24.60; H, 5.09. [c] For *ca.* 10^{-3} M solutions in 1,2-dichloroethane at 25°. Reference value under the same conditions is 17.0 for $[(n\text{-}C_4H_9)_4N]Br$. [d] For *ca.* 10^{-2} M solutions in 1,2-dichloroethane at 37°.

low-spin five-coordinated complexes ligands contain atoms of phosphorus in addition to sulfur[5] or the ligands are highly conjugated like dithiolates.[6] On the other hand, it has recently been reported[7] that thiourea (tu) forms high-spin complexes of the type $CoX_2 \cdot 3tu$, with X = Cl, Br. It therefore seemed interesting to study complexes formed by the potentially tridentate ligand bis(2-dimethylaminoethyl) sulfide (Me$_4$daes), $S[CH_2CH_2N(CH_3)_2]_2$,[4] which has an N$_2$S set of donor atoms. This ligand is structurally similar to $CH_3N[CH_2CH_2N(CH_3)_2]_2$,[3] Me$_5$dien, and $O[CH_2CH_2N(CH_3)_2]_2$,[4] Me$_4$daeo, which form high-spin five-coordinated complexes.

This paper contains a description of the compounds formed from Me$_4$daes with chlorides, bromides, and thiocyanates of cobalt and nickel. The stereochemistry of these compounds has been investigated by measurements of visible and infrared spectra, molecular weights, conductivities, and X-ray powder photographs.

Experimental Section

Preparation of the Compounds.—The preparation of bis(2-dimethylaminoethyl) sulfide was accomplished according to the procedure of Marxer and Miescher.[8] The metal compounds were prepared by mixing hot solutions of the appropriate metal salt (0.010 mole) in 1-butanol (60 ml) and of bis(2-dimethylaminoethyl) sulfide (0.012 mole) in 1-butanol. Concentration by distillation followed by cooling yielded the compound. The crystalline compounds were filtered in a closed system and dried in a moisture-free nitrogen stream. They were recrystallized by dissolving them in chloroform containing a few drops of Me$_4$daes and adding petroleum ether to the filtered solution. All of the compounds are very hygroscopic solids.

Physical Measurements.—The absorption spectra were recorded in the range 5000–30,000 cm^{-1} with a Beckman DK2 spectrophotometer equipped with a thermostated cell housing. Temperatures from 37 to 170° were obtained by circulating liquid from a thermostat regulating to ±0.5°. The solvents were of reagent grade quality and were dried and distilled before use. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentration of the solutions were approximately 10^{-3} M.

Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. The solutions were approximately 2×10^{-2} M. The results were reproducible ±1%.

The apparatus and the experimental technique used for the magnetic measurements were described in a previous paper.[9]

The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer 337 spectrophotometer.

Results

The analytical data and some characteristics of the Me$_4$daes complexes are given in Table I. All of the compounds are soluble in nitroethane, 1,2-dichloroethane, chloroform, and low-boiling alcohols but are insoluble in nonpolar solvents.

Electric conductivity measurements on the solutions show that these compounds are essentially nonelectrolytes in 1,2-dichloroethane (Table I). In nitroethane solutions they show a slight conductivity which is a small fraction of that of typical 1:1 electrolytes—*e.g.*, in 10^{-3} M nitroethane solutions at 25°, molar conductances are 16 and 76 cm^2/ohm mole for Ni(Me$_4$daes)Br$_2$ and $[(n\text{-}C_4H_9)_4N]Br$, respectively. Measurements of molecular weight at 37° in 1,2-dichloroethane show that a proportion of associated species is present in solution. The degree of association $\bar{n} = M(\text{found})/M(\text{calcd})$ is 1.17–1.27 (Table I).

The magnetic moments of the complexes at room temperature (Table II) are typical of the high-spin configurations of cobalt(II) and nickel(II). The spectra of the compounds and of their solutions in 1,2-dichloroethane, *o*-dichlorobenzene, and nitroethane have been recorded at room temperature. The spectra of the solutions have also been recorded at elevated temperatures (to 70 and 170° for 1,2-dichloroethane and *o*-dichlorobenzene, respectively).

The infrared spectra of the isothiocyanate complexes show two ν(CN) stretching vibrations at 2070 and 2090 cm^{-1} for Co(Me$_4$daes)(NCS)$_2$ and at 2075 and 2095 cm^{-1} for Ni(Me$_4$daes)(NCS)$_2$. Characteristic C–S stretching frequencies occur at 820 cm^{-1} for the cobalt complex and at 808 and 812 cm^{-1} for the nickel analog. These frequencies are indicative of an N-bonded NCS group.[10] The two C–N and C–S stretching absorption bands are probably due to the lack of the center of sym-

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(5) G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965); G. Deischer and O. Schwarzenbach, *Helv. Chim. Acta*, **49**, 1927 (1966).

(6) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(7) K. C. Dash and D. V. R. Rao, *Z. Anorg. Allgem. Chem.*, **345**, 217 (1966).

(8) A. Marxer and K. Miescher, *Helv. Chim. Acta*, **34**, 924 (1951).

(9) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(10) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960); A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

TABLE II

MAGNETIC DATA FOR SOME COMPLEXES IN THE SOLID STATE

Compd	Temp, °C	$10^6\chi_g$, cgsu		μ_{eff}, BM
$Co(Me_4daes)Cl_2$	19	28.0	8760	4.55
$Co(Me_4daes)Br_2$	18	21.1	8530	4.50
$Co(Me_4daes)(NCS)_2$	18	23.2	8380	4.44
$Ni(Me_4daes)Cl_2$	19	14.0	4460	3.24
$Ni(Me_4daes)Br_2$	18	11.1	4580	3.30
$Ni(Me_4daes)(NCS)_2$	18	12.8	4700	3.32

metry in these compounds which makes both the symmetric and antisymmetric modes infrared active.

X-Ray powder photographs of the complexes of cobalt and nickel with the same anion are almost indistinguishable. The compounds are probably isomorphous. The relevant X-ray powder data are available through the ASTM file.

Discussion

The three complexes $Co(Me_4daes)X_2$, with X = Cl, Br, NCS, have diffuse reflectance spectra which are clearly diagnostic of a five-coordinated structure. The present compounds may not possess regular trigonal-bipyramidal or square-pyramidal stereochemistries because of the difference of the donor atoms and the geometrical requirements of the chelate. These chromophores may have at most C_{2v} symmetry, which is a subgroup of both the groups C_{4v} and D_{3h}. Lacking X-ray structural data, qualitative assignments of the spectra of the compounds may be made tentatively by using the energy level diagrams which are valid for the two regular stereochemistries. We have used the diagrams for the point group D_{3h} because, first, these have been reported for cobalt(II) and nickel(II)[11] and, second, the effect of the descent in symmetry to C_{3v} has been studied.[12] The energy level diagrams for the point group C_{4v} have been reported only for the nickel(II) ion.[11]

The ligand field spectrum of $Co(Me_4daes)(NCS)_2$ is completely analogous to that of $[Co(Me_6tren)Br]Br$,[2] where $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$, for which a trigonal-bipyramidal chromophore CoN_4Br (strictly of the point group C_{3v}) has been ascertained by X-ray crystallography.[13] These spectra are compared in Figure 1. The only essential difference is that the bands of the compound $Co(Me_4daes)(NCS)_2$ are displaced toward higher frequencies by a few hundred wavenumbers when compared with those of $[Co(Me_6tren)Br]Br$. This is in accordance with the fact that a stronger ligand field is created by thioether sulfur[14] than by bromide and with NCS groups coordinated *via* the nitrogen (chromophore CoN_4S). Infrared data also indicate the N-bonded coordination. In accordance with the assignment of other spectra of five-coordinated complexes of cobalt, completed in a previous paper,[4] the bands shown by $Co(Me_4daes)(NCS)_2$ at 6000, 12,500, 16,500, and 19,400 cm^{-1} are tentatively assigned to the four spin-allowed transitions (point group D_{3h}): $^4A'_2(F) \rightarrow {}^4E''(F)$, $^4E'(F)$, $^4A'_2(P)$, and $^4E''(P)$, respectively.

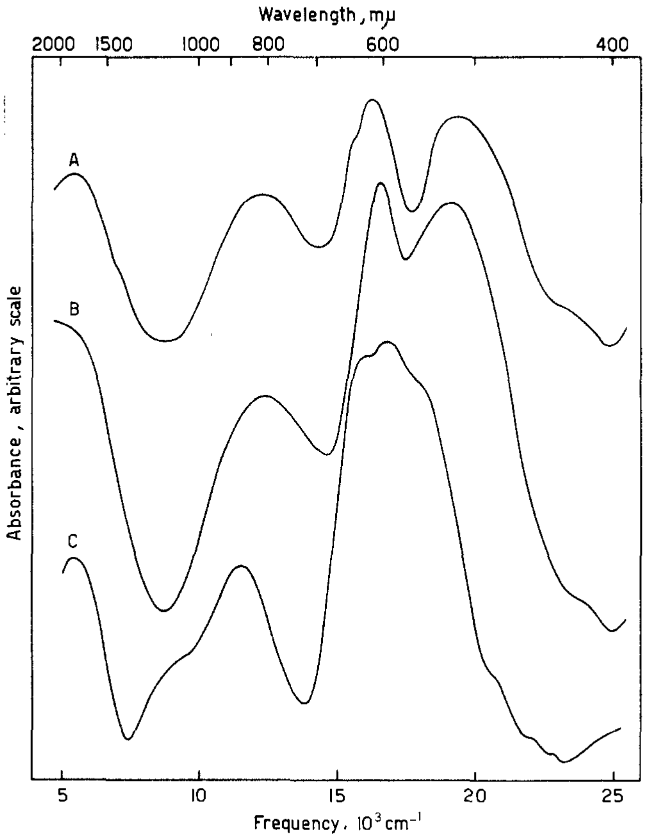

Figure 1.—Diffuse reflectance spectra of some five-coordinated high-spin complexes of cobalt(II): A, $[Co(Me_6tren)Br]Br$; B, $Co(Me_4daes)(NCS)_2$; C, $Co(Me_4daes)Br_2$.

The spectra of the chloride and bromide of cobalt with Me_4daes are almost identical but differ from the spectrum of the isothiocyanate in some details. For example, the $^4A'_2(F) \rightarrow {}^4E'(F)$ transition is split into two components (Figure 1). These components are at lower frequencies than for the analogous isothiocyanate. The band also behaves in a similar way in other compounds with low symmetry, *e.g.*, $Co(Me_5dien)Cl_2$,[3] the distorted trigonal-bipyramidal structure of which has been ascertained by an X-ray investigation.[15] Furthermore, the $^4A'_2(F) \rightarrow {}^4E''(P)$ band is also split and shifted toward the red so that it converges with the $^4A'_2(F) \rightarrow {}^4A_2'(P)$ band. It has already been noted[4] how displacement toward the red and splitting of these two bands is in accordance with the large field-strength dependence and the degenerate nature of the excited $^4E'(F)$ and $^4E''(P)$ levels, respectively. As expected, the transition to the excited $^4A'(P)$ level is, however, rather insensitive to field strength.[4] It is therefore reasonable to attribute the slight spectral differences between these halogen complexes and the analogous isothiocyanate to the lower symmetry of the ligand field in the first two complexes, caused essentially by the disparity of the donor atoms. On the other hand, the spectral characteristics of high-spin cobalt(II) compounds with different stereo-

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[11] M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

[12] M. Ciampolini, submitted for publication.

[13] M. Di Vaira and P. O. Orioli, *Inorg. Chem.*, **6**, 490 (1967).

[14] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[15] M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

chemistries (*i.e.*, octahedral and tetrahedral) are distinctly different.[16] A five-coordinated structure has therefore been assigned to these three compounds in the solid state.

Fivefold coordination is also found for the Ni(Me$_4$daes)X$_2$ complexes, with X = Cl, Br, NCS. The spectra of these nickel complexes are, in fact, distinctly similar to those of high-spin five-coordinated complexes like [Ni(Me$_6$tren)Br]Br.[2] These spectra are compared in Figure 2. In the case of the compound Ni(Me$_4$daes)(NCS)$_2$ all of the peaks are displaced toward higher frequencies by about 500 cm^{-1} compared with [Ni(Me$_6$tren)Br]Br, in accordance with its isothiocyanate formulation. The ratio between the frequencies of the first two more intense peaks—7600 and 15,000 cm^{-1}—is about 2.[2] These two peaks can, in accordance with previous work,[4] be assigned to the transitions $^3E'(F) \rightarrow {}^3E''(F)$ and $^3A'_2$, respectively, if a D$_{3h}$ symmetry is assumed. Another intense band which is found at 23,500 cm^{-1} can similarly be assigned to the transitions $^3E'(F) \rightarrow {}^3E''(P)$. Other weaker bands and shoulders are present, as may be expected from the energy level diagram.[11]

When the isothiocyanate is substituted by chloride and bromide, all of the bands are displaced toward lower frequencies (Figure 2) in accordance with the positive slope of the plot of the energy of the excited levels against the field strength. The first transition, *i.e.*, $^3E'(F) \rightarrow {}^3E''(F)$, is neatly split into two components. The spectra of these nickel complexes are therefore interpretable in terms of a five-coordinated structure of low symmetry.

It may be concluded that the thioether group may also be present in five-coordinated complexes of the high-spin type. This behavior is in accordance with the position of thioether sulfur between water and ammonia in the spectrochemical series.[14] The contribution of sulfur to the strength of the ligand field is therefore smaller than that of nitrogen. However, the situation is complicated by the fact that sulfur, if it produces a large nephelauxetic effect, might cause spin pairing.[11] The position of sulfur in the nephelauxetic series has not yet been determined unambiguously.[14,17]

Behavior in Solution.—When these cobalt and nickel complexes are dissolved in noncoordinating solvents, such as 1,2-dichloroethane, they are predominantly monomeric entities M(Me$_4$daes)X$_2$. There is no appreciable electrolytic dissociation but a rather large fraction of molecules is present as associated species (Table I). These species may be formulated as octahedral dimers. The association may take place *via* bridges of halogen and thiocyanate ions or by sharing sulfur atoms.[18]

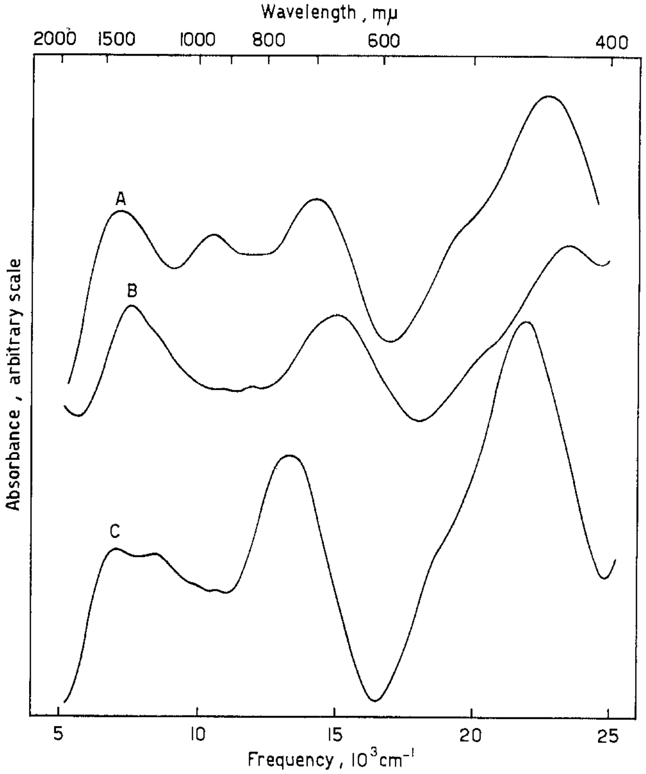

Figure 2.—Diffuse reflectance spectra of some five-coordinated high-spin complexes of nickel(II): A, [Ni(Me$_6$tren)Br]Br; B, Ni(Me$_4$daes)(NCS)$_2$; C, Ni(Me$_4$daes)Br$_2$.

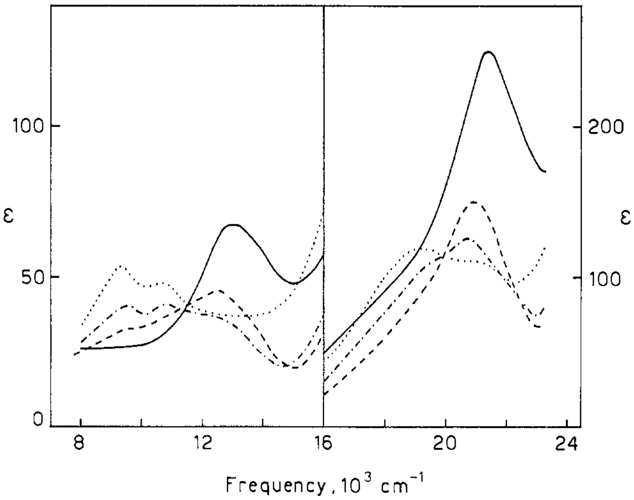

Figure 3.—Temperature dependence of the absorption spectra of Ni(Me$_4$daes)Br$_2$ in *o*-dichlorobenzene: ———, 25°; – – – –, 100°; - · - ·, 135°; ······, 170°.

It is noticeable that the absorption spectra in 1,2-dichloroethane or *o*-dichlorobenzene, at room temperature, are essentially similar to the diffuse reflectance spectra of the respective solids. The absorption due to the associated species must therefore be weak compared with that from the monomeric five-coordinated species. This is consistent with their proposed octahedral stereochemistry.

Increasing the temperature of the solutions leads to a decrease of the bands characteristic of the five-coordinated species and to the appearance of new bands.

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[16] C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955); S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960); F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961); J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

[17] S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

[18] A referee has pointed out that dipole–dipole type association between individual complexes could occur without change in coordination number. Such an explanation of the molecular weight data is also consistent with the solution spectra.

The spectral changes for the solution of Ni(Me$_4$daes)Br$_2$ in *o*-dichlorobenzene, from room temperature to 170°, are shown in Figure 3. The new bands at 14,900 and 16,700 cm^{-1} for the cobalt complex and at 9300, 10,700, and 19,300 cm^{-1} for the nickel complex are characteristic of distorted tetrahedral species of these two elements. In fact, these bands are also shown by tetrahedral ML$_2$X$_2$ complexes, where M = Co, Ni; L = $(CH_3)_2N(CH_2)_nN(CH_3)_2$, with $n = 2, 3$; X = Cl, Br.[19] In the solutions of the Ma$_4$daes complexes there are, therefore, also distorted tetrahedral species, the percentage of which increases with increasing temperature.

Acknowledgment.—Thanks are expressed to Professor L. Sacconi for helpful discussions. We are indebted to Dr. N. Nardi for experimental assistance. The financial support of the Italian "Consiglio Nazionale delle Ricerche" is gratefully acknowledged.

(19) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).

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The Crystal and Molecular Structure of an Oxo-Bridged Binuclear Iron(III) Complex, [(HEDTA)FeOFe(HEDTA)]$^{2-}$

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The crystal and molecular structure of ethylenediammonium N-hydroxyethylethylenediaminetriacetatoiron(III)-μ-oxo-N-hydroxyethylethylenediaminetriacetatoferrate(III) hexahydrate, (enH$_2$)[(HEDTA)FeOFe(HEDTA)]·6H$_2$O, has been determined by a three-dimensional X-ray crystallographic analysis. The compound crystallizes as bright red prisms in space group P2$_1$/c with unit cell dimensions a = 18.22, b = 11.50, c = 17.42 A, β = 103° 55′, and Z (for the dimer) = 4. From approximately 2350 independent nonzero reflections estimated visually from Weissenberg photographs, the structure was solved by the use of conventional Patterson, Fourier, and least-squares refinement techniques to a final value for the discrepancy index, R, of 0.114. The geometry of the anion consists of two Fe(HEDTA) moieties in which the HEDTA ligand is pentadentate. These are connected by an approximately linear oxo bridge (Fe–O–Fe = 165.0°), having relatively short Fe–O distances of 1.79 A. A qualitative molecular orbital description of the complex is presented.

Introduction

Recent studies of the spectral and magnetic properties of Fe(III)–EDTA, Fe(III)–HEDTA, and other related iron(III) systems, both in aqueous solution and in the solid state, have been interpreted in terms of a monomer–dimer equilibrium.[1,2] Among the compounds investigated was a low-spin Fe(III)–HEDTA complex which, primarily on the basis of its infrared spectrum and magnetic moment, was assigned the structure [(HEDTA)Fe–O–Fe(HEDTA)]$^{2-}$, where the HEDTA groups were thought to be pentadentate. Although linear metal–oxygen–metal groups have been proposed frequently in the past to account for certain properties of first-row transition metal complexes,[3] few have been structurally characterized by X-ray diffraction.[4–7] It was therefore of interest to us to determine the X-ray structure of the crystalline compound (enH$_2$)[(HEDTA)FeOFe(HEDTA)]·6H$_2$O reported earlier.[1,2] The results, which are presented here, fully corroborate the previous structural assignment and, in addition, provide new information concerning the nature of the bonding in this and related complexes containing linear M–O–M groupings.

Experimental Procedures and Results

Collection and Reduction of X-Ray Data.—The compound was prepared as described previously[1] and recrystallized from a hot dimethylformamide–water solution. The crystal used in all X-ray studies reported here was a small red prism having a mean cross section of 0.1 mm. Airplane glue was used to mount the crystal on the end of a glass fiber along the b axis. After an approximate optical alignment, the crystal was transferred to the precession camera where the space group and unit cell dimensions were determined using Zr-filtered Mo Kα radiation (λ 0.7107 A). The density was measured by flotation in a mixture of carbon tetrachloride and chloroform.

Intensity data were collected on the Weissenberg camera using molybdenum radiation filtered through zirconium. With this radiation, the linear absorption coefficient μ was calculated to be 9.47 cm^{-1}, resulting in a value of 0.047 for $\mu R_{\max}$. Since the maximum effect of absorption on the intensities was estimated to be less than 2%, no absorption corrections were applied. The intensities of approximately 2350 nonzero reflections, for which

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(1) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967).

(2) EDTA = ethylenediaminetetraacetate; HEDTA = N-hydroxyethylethylenediaminetriacetate; enH$_2^{2+}$ = ethylenediammonium cation.

(3) Examples include: (a) titanium: K. Watenpaugh and C. N. Cauglan, *Inorg. Chem.*, **6**, 963 (1967); (b) vanadium: T. W. Newton and F. B. Baker, *ibid.*, **3**, 569 (1964); (c) chromium: A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961); (d) manganese: L. H. Vogt, A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966); (e) iron: G. Anderegg, *Helv. Chim. Acta*, **45**, 1643 (1962), and ref 1 and 3b.

(4) *Cf.* ref 3a and 3d. Also, note the recent communication by E. Fleischer and J. Hawkinson, *J. Am. Chem. Soc.*, **89**, 721 (1967), which reports the structure of a seven-coordinate Fe(III) dimer containing macrocyclic, polydentate ligands.

(5) Several structural studies of second- and third-row transition metal complexes containing M–O–M groups have been carried out, *e.g.*, [Cl$_5$RuORuCl$_5$]$^{4-}$ [6] and [Cl$_5$ReOReCl$_5$]$^{2-}$.[7]

(6) A. M. Matheson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

(7) J. C. Morrow, *ibid.*, **15**, 851 (1962).