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Circular Dichroism of Coordination Compounds. V. Pentadentate Ethylenediaminetetraacetic Acid Complexes of Cobalt(III)[1]

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The absorption spectra, optical rotatory dispersion (ORD), and circular dichroism (CD) curves for complexes of the type $[Co(EDTA)X]^{2-}$ are reported, where X is Br^-, Cl^-, or NO_2^-. Although the ORD curves give some information regarding the absolute configuration of the complexes, the CD data were necessary to confirm the assignments. The D or Λ configuration was assigned to the $(+)_{546}$ isomers of $[Co(EDTA)Br]^{2-}$ and $[Co(EDTA)Cl]^{2-}$ and the $(-)_{546}$ isomer of $[Co(EDTA)NO_2]^{2-}$.

Introduction

In an earlier communication, the circular dichroism (CD) splitting patterns of the ethylenediaminetetraacetatocobaltate(III) ion, $[Co(EDTA)]^-$, have been discussed.[2] This complex contained the sexadentate EDTA ligand and approximated C_2 symmetry. In this paper some pentadentate complexes with EDTA are considered. These have the general formula $[Co(EDTA)X]^{2-}$, where X is Br^-, Cl^-, or NO_2^- and one of the carboxylate groups of the EDTA ligand is uncoordinated. This arrangement is supported by the results of infrared investigations of these complexes.[3] The compounds may also exist in an acidic form, of the general formula $[Co(HEDTA)X]^-$, where the free carboxylate group is protonated and the acid dissociation constant for each of these complexes has $pK_a \simeq 3$.[4-7] The chloro and bromo complexes are rather labile in solution and a dissociation reaction occurs at an appreciable rate whereby the X group is eliminated and the hexacoordinated EDTA species is formed. The kinetics of this reaction have been investigated and when the pH ≤ 7, a first-order reaction has been indicated.[6-10]

These complexes may exist in two geometrical arrangements, depending on whether the X group is *trans* to either a nitrogen or oxygen atom. Although there is some evidence that the racemic bromo complex might be a mixture of both isomers,[9] the resolved complex seems to consist only of one form as evidenced by the fact that both optical isomers have been obtained with equal magnitudes of rotation, and conversion reactions may occur for both isomers with complete retention of configuration.[11] There is no evidence for the presence of more than one geometrical isomer for the chloro and nitro complexes.

These complexes all have C_1 molecular symmetry. The effective crystal field symmetry, which considers only the atoms bonded to the metal ion, would be tetragonal or rhombic, depending on the crystal field strength and position of the X group. Thus one might expect to be able to distinguish between the two possible isomers on the basis of splittings observed in the absorption spectra. However, splitting is observed for one band only for the nitro compound. It has been shown that optical rotatory dispersion (ORD) and CD curves often reveal splittings which are not at all apparent from the absorption curves.[2] The ORD and CD data can be expected to provide more information regarding the stereochemistry of such complexes than the absorption data.

Experimental

The resolving agent used for all the complexes was an enantiomer of *cis*-dinitrobis(ethylenediamine)cobalt(III) bromide and both optical isomers were obtained in all cases. The resolved complex disodium bromo(ethylenediaminetriacetatoacetate)cobaltate(III) tetrahydrate, $Na_2[Co(EDTA)Br] \cdot 4H_2O$, was prepared by the methods of Schwarzenbach[4] and Dwyer and Garvan[11]; $[\alpha]_{546}$ ±800°, observed and reported. The resolved

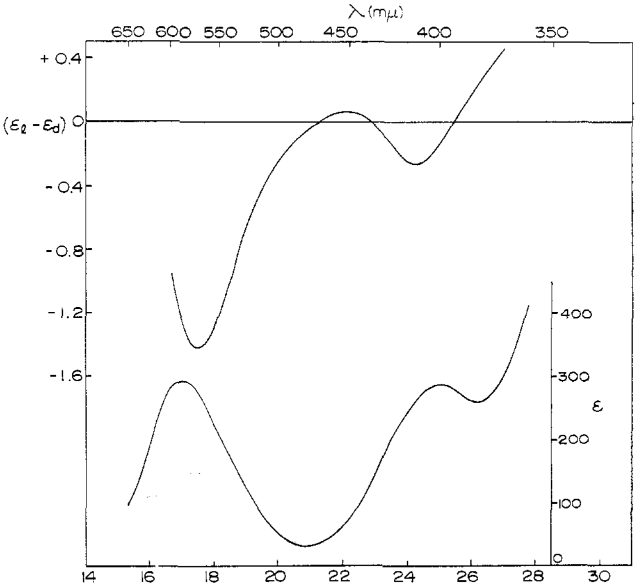

Figure 1.—Circular dichroism and molar absorptivity *vs.* wave number for $(+)_{546}$-$Na_2[Co(EDTA)Br] \cdot 4H_2O$.

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[1] This work was supported by a research grant (GM10829-06) from the Division of General Medical Studies, Public Health Service.

[2] B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

[3] M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

[4] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

[5] G. Schwarzenbach and J. Heller, *ibid.*, **34**, 576 (1951).

[6] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).

[7] R. Dyke and W. C. E. Higginson, *ibid.*, 2788 (1963).

[8] I. A. W. Shimi and W. C. E. Higginson, *ibid.*, 260 (1958).

[9] M. L. Morris and D. H. Busch, *J. Phys. Chem.*, **63**, 340 (1959).

[10] W. C. E. Higginson and M. P. Hill, *J. Chem. Soc.*, 1620 (1959).

[11] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

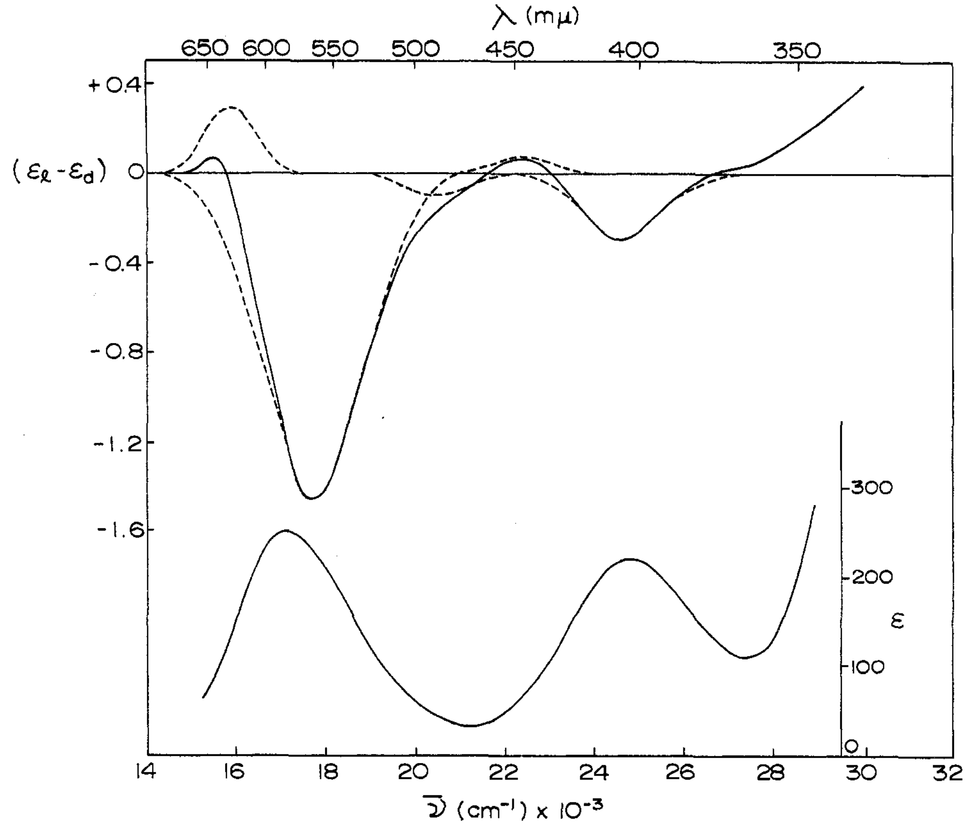

Figure 2.—Circular dichroism and molar absorptivity *vs.* wave number for $(+)_{546}$-$K_2[Co(EDTA)Cl] \cdot 3H_2O$: observed curve (———), gaussian analysis (- - - -).

isomers of dipotassium chloro(ethylenediaminetriacetatoacetate)cobaltate(III) trihydrate, $K_2[Co(EDTA)Cl] \cdot 3H_2O$, were prepared and resolved by the method of Dwyer[11]; $[\alpha]_{546}$ ±700°, observed and reported. Disodium nitro(ethylenediaminetriacetatoacetate)cobaltate(III) trihydrate, $Na_2[Co(EDTA)NO_2] \cdot 3H_2O$, was also prepared by Dwyer's methods[11]; $[\alpha]_{546}$ ±700°, observed and reported.

The absorption spectra were measured on a Cary Model 14 recording spectrophotometer. Optical rotations for the ORD curves were obtained using a Rudolph Model 80Q6 polarimeter with quartz optics and a photoelectric attachment. A 100-watt zirconium arc lamp was used in the visible region and a Rudolph Model 614 xenon arc lamp below 400 mμ. The CD curves were recorded with a Roussel–Jouan Dichrograph at wave lengths less than 600 mμ.

All measurements were made in aqueous solution at room temperature for the optically active doubly negative anion. The concentrations of the samples varied from 2×10^{-3} to 6×10^{-3} *M* and the cells used were either 1, 2, or 5 cm. in length. When information was needed for the acidic form of the complex, 0.1 *N* HCl was used as the solvent. The results obtained in this manner also agreed with what was found using the solid acidic form dissolved in acid. The solid acidic form of each complex ($pK_a \sim 3$) dissolved in water is appreciably dissociated to give the doubly negative anion.

Results

The circular dichroism curves and absorption spectra for these complexes are shown in Figures 1–3. The bromo compound has two absorption peaks at 17,050 cm.$^{-1}$ (ε 293) and 25,050 cm.$^{-1}$ (ε 282), while the chloro compound has two peaks at 17,100 cm.$^{-1}$ (ε 250) and 24,750 cm.$^{-1}$ (ε 221). The molar absorptivity values, ε, are in l. mole^{-1} cm.$^{-1}$. The relative positions of the long wave length band are consistent with what would be predicted from the spectrochemical series. The nitro compound, however, shows two peaks in the region of this absorption band, at 17,100 cm.$^{-1}$ (ε 116) and 20,050 cm.$^{-1}$ (ε 236). Evidently the crystal field splitting caused by the NO_2^- group is sufficiently strong to cause an appreciable splitting of the levels. A peak is also evident at 29,400 cm.$^{-1}$ (ε 3410).

The CD curve for the bromo compound has peaks at 17,500 cm.$^{-1}$ (−1.44), 22,100 cm.$^{-1}$ (+0.08), and 24,300 cm.$^{-1}$ (−0.27). (The values of the CD at the observed maxima are given in parentheses.) The chloro compound has CD peaks at 15,450 cm.$^{-1}$ (+0.05), 17,700 cm.$^{-1}$ (−1.48), 22,350 cm.$^{-1}$ (+0.07), and 24,650 cm.$^{-1}$ (−0.30). The nitro compound has CD peaks at 17,150 cm.$^{-1}$ (+1.01), 19,450 cm.$^{-1}$, (−1.13), a shoulder at 21,750 cm.$^{-1}$ (−0.42), a peak at 24,450 cm.$^{-1}$ (+0.25), and a broad band centered around 28,250 cm.$^{-1}$ (−0.90). Data were obtained for the chloro and nitro compounds at wave lengths beyond 600 mμ since these results were needed, particularly for the chloro compound, in order to make a gaussian analysis of the CD curve in the region of the first absorption band.[12] The results of this analysis[13]

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(12) The authors wish to express their appreciation to F. Woldbye, E. Larsen, and S. Bagger (Copenhagen) for making the CD measurements beyond 600 mμ.

(13) Parameters of CD peaks used for guassian analysis: chloro compound 15,900 cm.$^{-1}$ (+0.29, $\Delta\bar{\nu}$ 650 cm.$^{-1}$), 17,700 cm.$^{-1}$ (−1.48, $\Delta\bar{\nu}$ 1250 cm.$^{-1}$), 20,400 cm.$^{-1}$ (−0.09, $\Delta\bar{\nu}$ 800 cm.$^{-1}$), 22,400 cm.$^{-1}$ (+0.08, $\Delta\bar{\nu}$ 700 cm.$^{-1}$), and 24,650 cm.$^{-1}$ (−0.30, $\Delta\bar{\nu}$ 1,000 cm.$^{-1}$); nitro compound 17,150 cm.$^{-1}$ (+1.02, $\Delta\bar{\nu}$ 1150 cm.$^{-1}$), 19,350 cm.$^{-1}$ (−1.21, $\Delta\bar{\nu}$ 1000 cm.$^{-1}$), 21,450 cm.$^{-1}$ (−0.47, $\Delta\bar{\nu}$ 950 cm.$^{-1}$), and 24,750 cm.$^{-1}$ (+0.69, $\Delta\bar{\nu}$ 1050 cm.$^{-1}$).

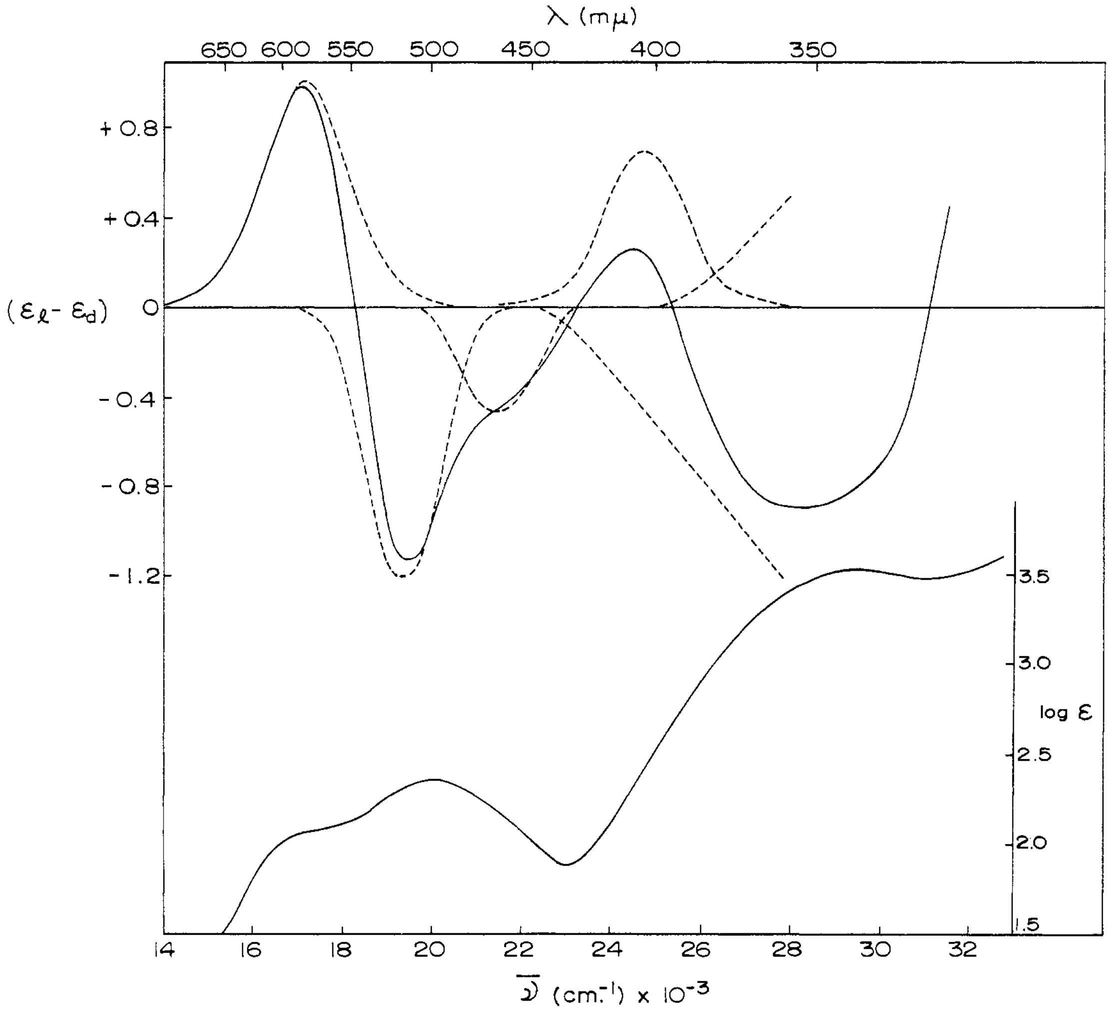

Figure 3.—Circular dichroism and molar absorptivity *vs.* wave number for $(-)_{546}$-$Na_2[Co(EDTA)NO_2]\cdot 3H_2O$: observed curve (———), gaussian analysis (- - - -).

of the CD curves are shown in Figures 2 and 3. The analysis is not complete in the high-frequency region since there is serious overlap with the charge-transfer band. In each case three components are indicated in the vicinity of the $^1A_{1g} \rightarrow {}^1T_{1g}$ region and the sign pattern is the same for both compounds, $(+, -, -)$. For the region of the second absorption band, the first CD peak is positive but the remaining pattern is uncertain because of the overlap with the very intense bands in the ultraviolet region. No gaussian analysis was made on the CD curve of the bromo complex since data were not available at longer wave lengths. However, the over-all similarity in the positions and magnitudes of the CD peaks of the chloro and bromo complexes is very striking and the results should be quite similar to those found for the chloro compound.

The ORD curves are compared in Figure 4. They have been reported previously for the chloro and nitro compounds,[14] but the curves presented here show somewhat more fine structure.

It is necessary to specify the solvent used in these cases since the curves obtained in acid solution have the same over-all shapes as those of the aqueous solutions but have slightly different magnitudes. The extinction coefficients of the doubly negative ions are approximately 10% higher than those for the acidic form for each complex. The magnitudes of the ORD and CD curves also vary for each form.

Discussion

The ORD curves compared in Figure 4 are believed to be for isomers with the same relative configuration. These curves are for the $(+)_{546}$ isomers of the chloro and bromo complexes and the $(-)_{546}$ isomer of the nitro compound. It was earlier thought that the $(+)_{546}$ isomers of the chloro and nitro complexes had the same configuration.[14] This was based partly on the solubility criterion that both of these isomers formed the less soluble diastereoisomer with $(-)_{589}$-*cis*-$[Co(en)_2(NO_2)_2]^+$ and partly because the ORD curves in the region of the first absorption band appeared to be rather similar. However, since the Cl^- and NO_2^- ions have much different crystal field strengths, the ORD curve of the chloro compound is shifted to longer wave lengths relative to that of the nitro compound, corresponding to the shifts observed for the absorption bands. The CD curves reveal that for the chloro

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[14] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 847 (1960).

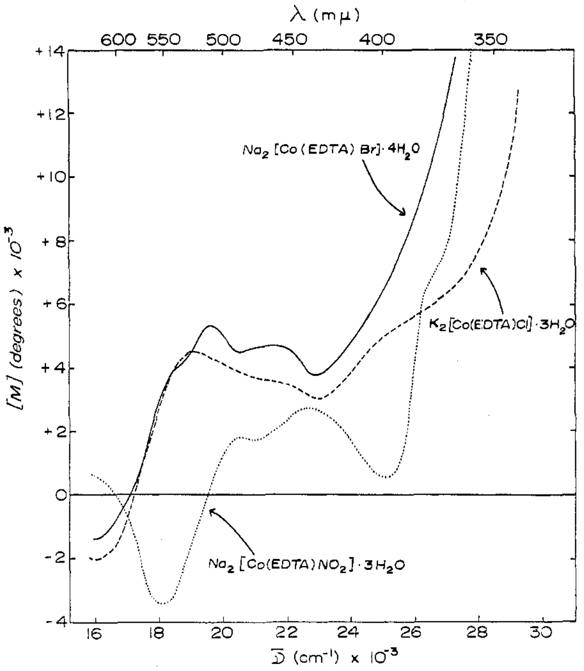

Figure 4.—Optical rotatory dispersion curves for the $(+)_{546}$ isomers of $Na_2[Co(EDTA)Br]\cdot 4H_2O$ and $K_2[Co(EDTA)Cl]\cdot 3H_2O$ and the $(-)_{546}$ isomer of $Na_2[Co(EDTA)NO_2]\cdot 3H_2O$

compound, the first component in the long wave length band is relatively weak compared to that for the nitro compound and the second CD band is by far the more dominant. This is reflected in the ORD curves and while the nitro compound has a typical V-shaped curve, suggesting two anomalous dispersion components of opposite sign, the chloro compound shows only the shape characteristic of one dominant component. It appears that the latter situation also prevails for the bromo complex. It is necessary to compare the over-all shape of these ORD curves at all wave lengths. In Figure 4 it can be seen that all the curves have approximately the same shape, although they are shifted relative to one another. This similarity is clearly seen in the high-frequency region, where all the curves show a large increase in positive rotation. It can be seen from the ORD curve for $(-)_{546}$-$[Co(EDTA)]^-$ that there is a sharp increase in this region also.[15] This corresponds to a contribution from the charge-transfer band. For complexes such as these, which are assumed to possess the same basic symmetry, it would be expected that this area of the curve might be a good indication of the relative configurations. The EDTA ligand should have almost the same arrangement about the metal for each complex of the same configuration, and the sign of this dominant component should be the same for those with the same relative configurations.

The CD curves give much clearer evidence for the fact that these complexes have the same relative configuration. The CD pattern is the same for all the complexes shown and also is the same as that for the $(-)_{546}$-$[Co(EDTA)]^-$ ion.[2] This over-all similarity suggests that these isomers may all be related to that of the $[Co(EDTA)]^-$ complex. The $(-)_{546}$ isomer of $[Co(EDTA)]^-$ was assigned the D or Λ absolute configuration, according to the convention suggested by Piper,[16] by comparing ORD and CD results.[2] Since these pentadentate complexes only involve a breaking and making of one metal–ligand bond, the arrangement of the EDTA ligand should remain basically the same. Therefore on the basis of the similarity of the ORD and CD curves, the D or Λ configuration may also be assigned to the $(+)_{546}$ isomers of $[Co(EDTA)Br]^{2-}$, $[Co(EDTA)Cl]^{2-}$, and the $(-)_{546}$ isomer of $[Co(EDTA)NO_2]^{2-}$. The orientation of the chelate rings in $[Co(EDTA)]^-$ relative to the spiral arrangement used in Piper's convention was shown earlier.[2]

This assignment is supported by the fact that it is known[11] that $(-)_{546}$-$[Co(EDTA)]^-$ is converted into $(+)_{546}$-$[Co(EDTA)Cl]^{2-}$. The reaction is completely reversible and occurs with complete retention of configuration. Further kinetic studies by Busch[17] give rise to the same conclusion.

For complexes with C_1 symmetry and a rhombic crystal field, it would be expected that both the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ bands should be split into three components, all of which are designated as A. In order to assign these bands, the $[Co(EDTA)]^-$ complex is useful for comparison although it is of higher symmetry, C_2, and has an A and two B components. The A component of this complex should be related to one of the three A components of the pentadentate complexes. The A component of $(-)_{546}$-$[Co(EDTA)]^-$ was designated as the first band and the CD peak was positive. It would be expected that the corresponding A component in the pentadentate complexes should also be positive for complexes of the same configuration. For each complex this corresponds to the first band also.

For the chloro and nitro complexes (and apparently also for the bromo complex, although data for this band were not available), the intensity of this first CD band is decreased relative to that for $[Co(EDTA)]^-$, perhaps because a chelate ring is lost on going from the sexadentate to the pentadentate complexes. Liehr's theory of optical activity predicts that in dihedral complexes, the rotational strength, which is directly proportional to the CD, increases upon chelation.[18] This is said to be due to a "mismatch" of the bonding orbitals because of the constraint of the chelate ring. Such an arrangement may also apply for these compounds. The $[Co(EDTA)]^-$ complex has five chelate rings, of which two are apparently strained.[19]

For all the complexes studied, it was found that three CD bands could be located in the region of the first absorption band, as was found for the $[Co(EDTA)]^-$ complex. On the basis of crystal field theory this is an indication of rhombic symmetry in the molecule, suggesting that the X group is *trans* to a nitrogen. Although this is the isomer which would be expected to be more readily formed, the CD results do not give

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(15) T. Bürer, *Helv. Chim. Acta*, **46**, 242 (1963).

(16) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(17) D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961).

(18) A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

(19) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

conclusive proof since they give an indication of the "true" molecular symmetry and not just the effective symmetry determined by considering the ligand atoms as point charges. The latter approach has been used for the interpretation of absorption spectra with apparent success in cases where the actual number of components cannot be seen. In some of these cases the splittings were revealed from ORD or CD data.[2]

Contribution from the Departments of Chemistry, University of Essex,
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The Crystal and Molecular Structure of Bis(acetylacetonato)nickel(II)

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A three-dimensional analysis of the crystal structure of bis(acetylacetonato)nickel(II) has established that the molecule is trimeric with octahedral coordination of each nickel ion. The Ni–Ni distances are 2.882 and 2.896 Å. (e.s.d. 0.018 Å.), the Ni–O bond lengths being of two main types and averaging 2.12 and 2.01 Å., respectively (e.s.d. 0.07 Å.). Data indicating that the structure is typical of a variety of nominally four-coordinate metal complexes are summarized while the crystal structure is discussed in relation to theories which appear to require some modification.

Experimental

Bis(acetylacetonato)nickel(II) was prepared by the reaction of nickel hydroxide (obtained from Analar nickel sulfate) with acetylacetone. The resulting blue-green hydrate was converted to the emerald-green anhydrous compound (m.p. 229–230°) by subliming it at 170–210° and a pressure of 0.2–0.4 mm., the water removed being absorbed on phosphorus pentoxide. There was a small amount of decomposition on sublimation, a brown residue being left. As bis(acetylacetonato)nickel(II) is easily hydrated and has a tendency to coordination by solvent molecules, recrystallization from solution was avoided, and crystals suitable for X-ray examination were prepared by slow sublimation under the conditions stated above. In this way well-shaped crystals up to 0.5 mm. long were prepared.

The crystals are orthorhombic, $a = 23.23 \pm 0.04$ Å., $b = 9.64 \pm 0.02$ Å., $c = 15.65 \pm 0.02$ Å.[2] The observed density (by flotation) is 1.455 ± 0.001 g./ml. (at 17°); the density calculated for 12 formula units $Ni(C_5H_7O_2)_2$ in the unit cell is 1.460 ± 0.008 g./ml. Systematic absences are: $(0kl)$ when l is odd and $(h0l)$ when h is odd, indicating space groups Pca2_1 or Pcam. Tests for pyroelectricity and piezoelectricity were negative, and a statistical survey of $(0kl)$ and $(h0l)$ intensities did not permit a conclusive choice between Pca2_1 and Pcam to be made. The subsequent analysis proved Pca2_1 to be correct. Forms well developed are $\{010\}$,$\{001\}$,$\{00\bar{1}\}$,$\{201\}$,$\{20\bar{1}\}$, and to a lesser degree $\{110\}$, the crystals appearing to be holohedral. Cleavage planes are (010) and (201). The crystals are optically positive with birefringence less than 0.008; the optic axis is approximately perpendicular to (201).

For intensity measurements, crystals were sealed in thin-walled soda glass tubes (approximately 0.03 mm. thick) to prevent hydration of the crystals by atmospheric moisture. Three-dimensional data were collected from two sets of oscillation photographs (5° oscillation ranges, overlapping by 2°) taken, using Cu Kα radiation, with a and c as oscillation axes. From these photographs the intensities of all $(0kl)$, $(h0l)$, and $(hk0)$ reflections present and of the stronger of the general (hkl) reflections were measured, 1073 in all. It is estimated that only those reflections with $|F|$ less than 16 (compared to the largest observed $|F| = 282$, for (010)) were neglected. The very strong intensities were measured from a short exposure rotation photograph, all intensities being estimated visually by comparison with a standard scale.

Crystals were sometimes found to decompose after being sealed. In these circumstances the use of oscillation photographs offered an advantage over the use of Weissenberg photographs, since they required comparatively short exposures (1 hr.) and any decomposition occurring would be soon detected. The linear absorption coefficient for Cu Kα is 24.7 cm.$^{-1}$; crystals with their largest dimension equal to 0.5 mm. were used and no absorption corrections were made.

Intensities were corrected for Lorentz and polarization factors using the chart for oscillation photographs constructed by Kaan and Cole.[4] Corrections to intensities of upper layer reflections for variation in spot size and oblique incidence of the diffracted ray on the film were made and intensities put on an absolute scale using Wilson's method and later through the comparison of observed and calculated structure factors.

Analysis of the Structure

At the start of the analysis space groups Pca2_1 and Pcam both had to be considered as it had not been possible to choose between them from the systematic absences or by statistical tests. Attempts were made first to locate the 12 nickel atoms in the unit cell, possible arrangements of which are: (i) in Pca2_1, 3 sets of 4 in general position 4a, (ii) in Pcam, 1 set of 8 in general position 8e and 1 set of 4 in special positions (either 4a-$\bar{1}$, 4b-$\bar{1}$, 4c-2, 4d-m), or (iii) in Pcam, 3 sets of 4 all in special positions (chosen from 4a, b, c, or d).

The selection of the correct arrangement and the deduction of the nickel atom positions was made from the three-dimensional Patterson function employing, in particular, Patterson–Harker sections and lines. In the line $P(0, 0, W)$ there is, apart from the origin peak, only one small peak at $W = {}^1/_2$, there being a smooth drop from the origin along most of the length of the line. This suggests strongly that the space

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(1) (a) Department of Chemistry, University of Essex, Colchester, Essex; (b) Department of Chemistry, University of Sheffield; (c) William Ramsay and Ralph Forster Laboratories, University College, London.

(2) Data were given in a previous publication[3] for a different orientation of the crystallographic axes. The space group $P2_1ab$ used there has been here reoriented to Pca2_1, the standard crystallographic setting.

(3) G. J. Bullen, *Nature*, **177**, 537 (1956).

(4) G. Kaan and W. F. Cole, *Acta Cryst.*, **2**, 38 (1949).