two isomers containing h^3-C_7H_7 moieties (Ia and Ib); however, on the evidence at hand one cannot eliminate the possibility of an equilibrium between conformers of an h^1-C_7H_7 derivative. It appears that a crystal structure determination may be necessary to distinguish between these alternatives.

Experimental Section

The compound was prepared by the method of King and Bisnette.[3] The solvents were commercially available: $CHCl_2F$, CCl_2F_2, Matheson; toluene-d_8, Merck and Co. The Freons were purified by trap-to-trap distillation before use. Particular attention must be paid to this purification to avoid impurities which have nmr spectra surprisingly similar to some of the resonances observed in metal–olefin derivatives. Especially poor in this respect is $CHCl_2F$, which has impurities giving resonances at δ 0.89, 1.33, 4.19, and 5.23 at 0°. All of these impurity resonances except that at δ 5.23 can be efficiently removed by trap-to-trap distillation.

The spectra were recorded at 100 MHz using a Varian Associates HA-100 instrument with a variable-temperature probe. The temperature was measured with a thermocouple placed in an nmr tube at the level of the receiver coil. Variable-temperature infrared spectra were obtained with a modified Barnes Engineering temperature cell and a Perkin-Elmer 421 spectrometer.

Acknowledgment.—I am indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Connecticut Research Commission (Grant RSA 68-5) for support of this work; the National Science Foundation for Grant GP 6938 which supplied the HA100; the Climax Molybdenum Corp. for a gift of molybdenum carbonyl; Professor Martin Saunders for supplying a program which carries out the matrix manipulations necessary for nmr line-shape calculations; and Drs. F. A. Cotton and C. R. Reich for making their results available prior to publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF QUEENSLAND, ST. LUCIA, 4067 QUEENSLAND, AND NATIONAL STANDARDS LABORATORY, DIVISION OF APPLIED PHYSICS, CSIRO, SYDNEY, NEW SOUTH WALES, AUSTRALIA

Absolute Configurations of 1,10-Phenanthroline and 2,2′-Bipyridine Metal Complexes

BY J. FERGUSON, C. J. HAWKINS, N. A. P. KANE-MAGUIRE, AND H. LIP

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The nonempirical circular dichroism method for determining the distribution of chelate rings in dissymmetric metal complexes, which is based on long-axis-polarized $\pi \rightarrow \pi^*$ ligand transitions, is reviewed and applied to some cobalt(III), chromium(III), and nickel(II) 1,10-phenanthroline and 2,2′-bipyridine complexes. It is found that the relative energies of the split components of these transitions for the bis and tris complexes are dependent on the metal ion and cannot be determined by the simple dipole–dipole interaction theory. However, the sign of the splitting was determined experimentally by comparing the centers of gravity of the absorption bands for the bis and tris complexes with those of the equivalent mono complexes. The absolute configurations determined in this way are compared with those from the empirical method based on the d–d transitions and are found to be in good agreement.

The chirality of the distribution of chelate rings in dissymmetric metal complexes has been determined by circular dichroism studies using two fundamentally different approaches. The most general method is an empirical one which has been developed on the assumption that the signs of the Cotton effects of magnetic dipole allowed d–d transitions are dependent upon the distribution of chelates and independent of the ligand atoms and the chelate ring parameters such as the angle between the coordinate bonds.[1,2] Mason and his coworkers have developed an alternative nonempirical approach based on ligand transitions and have applied it to tris complexes of 1,10-phenanthroline,[3,4] 2,2′-bipyridine,[4] acetylacetonate,[5] and catecholate.[6] Bosnich has extended the application to the bis complex *cis*-bis(pyridine)bis(1,10-phenanthroline)ruthenium(II).[7] Recently Mason and Norman have attempted[8] to correlate the two approaches for d-Co(phen)$_3^{3+}$ and also have studied mixed phenanthroline and bipyridine complexes of osmium.[9]

The crucial issue in the application of the nonempirical method lies in the assignment of the components of the ligand absorption bands for which the circular dichroism has been measured. For the tris complexes, electrostatic interactions between the three ligands remove the threefold degeneracy associated with electronic excitation energy on one of the ligands. As a result, there are two excited states, an A_2 state and a twofold degenerate E state, within the D_3 symmetry of the complex. For the bis complexes, the corresponding states are A and B for the C_2 symmetry of the

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[1] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[2] C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965).

[3] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 211 (1963).

[4] A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 259 (1964).

[5] E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

[6] J. Mason and S. F. Mason, *Tetrahedron*, **23**, 1919 (1967).

[7] B. Bosnich, *Inorg. Chem.*, **7**, 178 (1968).

[8] S. F. Mason and B. J. Norman, *Inorg. Nucl. Chem. Letters*, **3**, 285 (1967).

[9] S. F. Mason and B. J. Norman, *Chem. Phys. Letters*, **2**, 22 (1968).

TABLE I

DATA FOR COMPLEXES STUDIED: REFERENCES FOR METHODS OF PREPARATION, ROTATIONS, AND SPECTROSCOPIC DATA FOR THE LONG-AXIS-POLARIZED π–π^* LIGAND BAND

	$[\alpha]^{20}$D, deg		Center of	CD			Abs
Complex studied	Calcd	Obsd	grav, kK	λ^{-1}, kK	Δ_ϵ	Trans	conf
d-[Co(phen)$_3$](ClO$_4$)$_3$ · 3H$_2$O[a]	+796	+800	36.30	35.62	+222.0	A$_2$	L
				37.38	−145.0	E	
d-[Cr(phen)$_3$](ClO$_4$)$_3$ 2 · 5H$_2$O[a]	+1320	+1280	37.20	36.55	+179.7	E	D
				39.00	−114.3	A$_2$	
l-[Ni(phen)$_3$](ClO$_4$)$_2$ · 2H$_2$O[b]	−1463[c]	−1467	37.50	36.63	−1330		
				38.76	+615.8		
l-[Co(bipy)$_3$](ClO$_4$)$_3$ · 2H$_2$O[d]	...	−263	32.50	31.40	−111.1	A$_2$	D
				33.56	+62.12	E	
dl-[Cr(bipy)$_3$](ClO$_4$)$_3$ · 3H$_2$O[e]	...	...	32.50				
l-[Ni(bipy)$_3$](ClO$_4$)$_2$ · 2H$_2$O[f]	−480[g]	−670[g]	33.50	32.55	−406.6		
				35.39	+54.64		
l-[Co(phen)$_2$(ox)]ClO$_4$ · H$_2$O[h]	−680	−680	36.80	35.71	−16.05	A	L
				37.23	+32.42	B	
d-[Cr(phen)$_2$(ox)]ClO$_4$ · 2.5H$_2$O[h]	+855	+855	36.55	35.35	+47.09	A	D
				38.32	−25.49	B	
l-[Ni(phen)$_2$(bipy)](ClO$_4$)$_2$ · 2H$_2$O[i]	−1375	−1181		33.90	−227.40		
				36.63	−454.80		
				38.46	+242.56		
d^l-[Ni(phen)$_2$(en)]Cl$_2$ · 9H$_2$O	...	...	37.50				
l-[Co(bipy)$_2$(ox)]ClO$_4$ · H$_2$O[h]	−541	−541	33.00	31.44	−22.11	A	L
				33.62	+27.74	B	
l-[Cr(bipy)$_2$(ox)]Cl · 4H$_2$O[h]	−361	−361	32.95	32.26	−17.63	B	D
				34.35	+7.12	A	
d-[Ni(bipy)$_2$(phen)](ClO$_4$)$_2$ · 2H$_2$O[i]	+725	+772		32.57	+23.63		
				33.61	+19.82		
				37.38	−7.98		
dl-[Co(en)$_2$(phen)]Br$_3$[j]			36.60				
dl-K[Cr(ox)$_2$(phen)][k]			36.30				
dl-[Ni(en)$_2$(phen)]Cl$_2$ · 5H$_2$O			37.50				
dl-[Co(en)$_2$(bipy)](ClO$_4$)$_3$[l]			32.75				
dl-K[Cr(ox)$_2$(bipy)] · 0.5H$_2$O[k]			33.10				
dl-[Ni(en)$_2$(bipy)]Cl$_2$ · 4H$_2$O			33.50				

[a] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Hunt, *Inorg. Chem.*, **5**, 1397 (1966). [b] G. B. Kauffman and L. T. Takahashi, *Inorg. Syn.*, **8**, 227 (1966). [c] At 15°. [d] Present work. [e] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952). [f] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1950). [g] At 5460 Å. [h] J. A. Broomhead, M. Dwyer, and N. A. P. Kane-Maguire, *Inorg. Chem.*, **7**, 1388 (1968). [i] J. A. Broomhead, Ph.D. Thesis, Australian National University, 1961. [j] A. Ablov, *Bull. Soc. Chim. France*, **4**, 1783 (1937). [k] J. A. Broomhead, *Australian J. Chem.*, **15**, 228 (1962). [l] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

molecule. While there have been no systematic attempts to examine the magnitudes and the signs of the splittings, it is often assumed that the relative energy order can be obtained by using the dipole–dipole approximation for the intermolecular potential. This approach places the B component at higher energy for the bis complexes and the A$_2$ component at higher energy for the tris complexes. However, this model takes no account of the role of the metal ion and it simply treats the sum total of the interactions as a simplified electrostatic one between the ligands. McCaffery, Mason, and Norman[4] have proposed that there is a difference in the sign of the splitting for tris(1,10-phenanthroline) and tris(2,2′-bipyridine) complexes of nickel(II), iron(II) and -(III), ruthenium(II) and -(III), and osmium(II) and -(III) based on diastereoisomer solubility and physiological specificity correlations of absolute configuration and the observed circular dichroism spectra. They rationalized this by considering differences in π bonding for the two ligands. However, in Mason and Norman's more recent paper[9] they have concluded that for the osmium complexes the signs of the splitting are identical for the two ligands.

In the present paper it is our aim to examine this basic problem for a series of metal complexes involving chromium(III), cobalt(III), and nickel(II) with 1,10-phenanthroline and 2,2′-bipyridine. An attempt is made to assign the order of energies based on an analysis of the absorption data. These assignments are used to arrive at configurations for the complexes and these configurations are then compared with those deduced from the empirical method.

Experimental Section

Preparation of Complexes.—Most of the complexes were prepared according to methods from the literature. The preparations of *l*-tris(2,2′-bipyridine)cobalt(III), *dl*-ethylenediaminebis(1,10-phenanthroline)nickel(II), *dl*-bis(ethylenediamine)mono(1,10-phenanthroline)nickel(II), and *dl*-bis(ethylenediamine)mono(2,2′-bipyridine)nickel(II), which have not been reported previously, are described below. All of the complexes used in this study are listed in Table I with the references for the methods of preparation and their rotations where appropriate.

l-Tris(2,2′-bipyridine)cobalt(III) Perchlorate Dihydrate.—An intimate mixture of cobalt chloride hexahydrate (0.48 g, 0.002 mol) and 2,2′-bipyridine (1.58 g, 0.01 mol) was dissolved in hot degassed water (35 ml). Solid sodium d-tartrate was added (12 g) and the solution was heated and stirred until the salt had dissolved. The solution was allowed to cool to room temperature and then was cooled in an ice bath. A greenish yellow precipitate was filtered and sucked dry. This tris(2,2′-bipyridine)cobalt(II) d-tartrate diastereoisomer (1.8 g) was suspended in carbon tetrachloride (120 ml) and chlorine was bubbled through the suspension while it was stirred for 70 min. The chlorine-saturated solution was decanted off and the remaining solvent was evaporated on a steam bath under an air stream. The solid was extracted with water (20 ml), the solution was filtered, and sodium perchlorate (5 g) was added to the filtrate. The yellow product (0.8 g), which precipitated almost immediately, was filtered off and washed well with cold, concentrated aqueous sodium perchlorate solution, cold 50% ethanol, ethanol, and finally ether; $[\alpha]^{20}D$ −263° (0.05% aqueous solution). *Anal.* Calcd for $[CoC_{30}H_{24}N_6](ClO_4)_3 \cdot 2H_2O$: C, 41.8; H, 3.3; N, 9.8; Cl, 12.3. Found: C, 42.1; H, 3.3; N, 9.9; Cl, 12.3.

dl-Ethylenediaminebis(1,10-phenanthroline)nickel(II) Chloride.—Two equivalents of 1,10-phenanthroline (2 g) was added to an ice-cold solution of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (1.8 g) (prepared according to the method of State[10]) in absolute ethanol. The solution was shaken for 10 min and was then filtered. The pink product was precipitated by adding ether to the filtrate, was washed well with ether, and was air dried. *Anal.* Calcd for $[NiC_{26}H_{24}N_6]Cl_2 \cdot 9H_2O$: C, 43.8; H, 6.0; Ni 8.2. Found: C, 43.3; H, 6.0; Ni, 8.2.

dl-Bis(ethylenediamine)mono(1,10-phenanthroline)nickel(II) Chloride.—$Ni(phen)Cl_2$ (2.4 g) (prepared according to the method of Broomhead and Dwyer[11]) was treated with a stoichiometric amount of ethylenediamine (1.2 ml) in ice-cold absolute ethanol. The flask was stoppered and shaken for 6 min, after which the solution was filtered and ether was added to the filtrate to precipitate the purplish red product, which was filtered, washed with ether, and air dried. *Anal.* Calcd for $[NiC_{16}H_{24}N_6]Cl_2 \cdot 5H_2O$: C, 37.0; H, 6.6; Ni, 11.3. Found: C, 37.2; H, 6.6; Ni, 11.2.

dl-Bis(ethylenediamine)mono(2,2′-bipyridine)nickel(II) Chloride.—This was prepared from $Ni(bipy)Cl_2$[11] by the same method as for the equivalent 1,10-phenanthroline complex. *Anal.* Calcd for $[NiC_{14}H_{24}N_6]Cl_2 \cdot 4H_2O$: C, 35.2; H, 6.8; Ni, 12.3. Found: C, 34.5; H, 6.7; Ni, 12.1.

Absorption and Circular Dichroism Spectra.—The absorption and circular dichroism spectra, which were measured with a Cary 14 spectrophotometer and a Roussel-Jouan Model B Dichrograph with a maximum sensitivity of 1.5×10^{-5}, respectively, are recorded in Figures 1–3. The spectra of the nickel(II) complexes were measured at approximately 0° in alcohol and fresh solutions were prepared for different parts of the spectral range so that any dissociation would be minimized. The ultraviolet spectra of the tris, bis, and mono complexes per mole of the ligand of interest are compared in Figures 4–6. In every case there is appreciable hypochromism associated with the bis and the tris spectra relative to the mono complex but this aspect of the problem will not be pursued in the present paper. In Figure 6 the spectra of the nickel complexes are given simply in terms of arbitrary optical density units. This is because the complexes containing ethylenediamine are relatively unstable in solution and their spectra were measured quickly in ethanol at 0° without weighing. However, as we are primarily interested in the location of the centers of gravity of the bands, values of the extinction coefficients are not essential to our analysis.

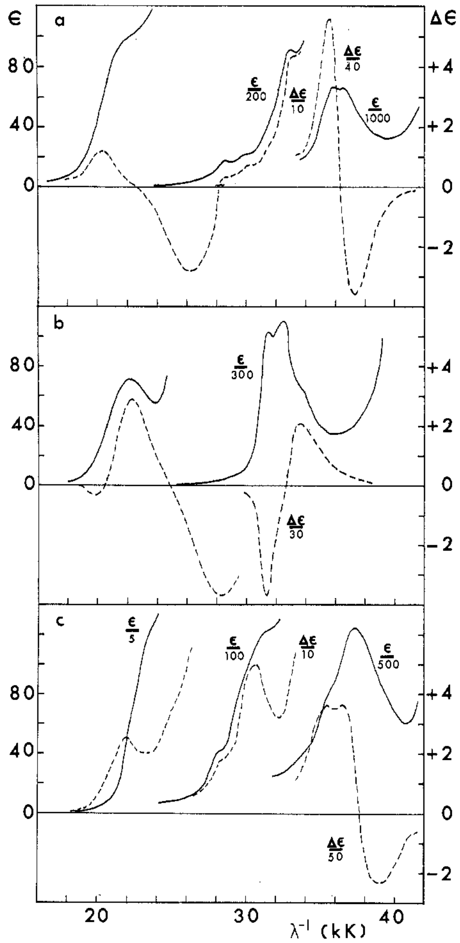

Figure 1.—Absorption (——) and circular dichroism spectra (---) of (a) d-$Co(phen)_3^{3+}$, (b) l-$Co(bipy)_3^{3+}$, and (c) d-$Cr(phen)_3^{3+}$ in aqueous solution.

The absorption transitions of major interest are those corresponding to the long-axis polarization of the ligands, which for 1,10-phenanthroline is the band near 37,000 cm^{-1} and for 2,2-bipyridine is the band near 33,000 cm^{-1}.[12] The centers of gravity of these bands were estimated by using a planimeter. A smooth continuous background was drawn under each band connecting the low- and high-energy sides of the band. For the 1,10-phenanthroline complexes with cobalt(III) and chromium(III) the contribution from the short-axis transition on the low-energy side of each band was subtracted. For the bipyridine complexes of chromium(III) a low-energy transition, probably a charge-transfer band, was subtracted. Centers of gravity of the mixed (1,10-phenanthroline)(2,2′-bipyridine)nickel(II) complexes were not obtained because of the difficulty in estimating the integrated overlapping band intensities. The centers of gravity are collected in Table I and they are indicated in Figures 4 and 5 by vertical lines at the bottom of each graph proportional to the number of ligands. The circular dichroism data for the two components are summarized also in Table I.

Attempts were made to determine the spectra of the various

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[10] H. M. State, *Inorg. Syn.*, **6**, 200 (1960).

[11] J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.*, **14**, 250 (1964).

[12] It has to be assumed that the majority of the intensity in both regions does in fact arise as a result of a transition polarized along the long molecular axis in each case. For 1,10-phenanthroline we have to rely on the calculations of Platt's perimeter model (J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949)) and its elaborations (W. Moffitt, *ibid.*, **22**, 320 (1954); N. S. Ham and K. Ruedenberg, *ibid.*, **25**, 13 (1956); E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1 (1963)) for the parent hydrocarbon, phenanthrene. These indicate that the transition is polarized along the long molecular axis. Similarly for 2,2′-bipyridine we rely on the recent calculation by Gondo (Y. Gondo, *J. Chem. Phys.*, **41**, 3928 (1964)), who used the Pariser-Parr method. This calculation indicates that the transition is polarized along the long axis.

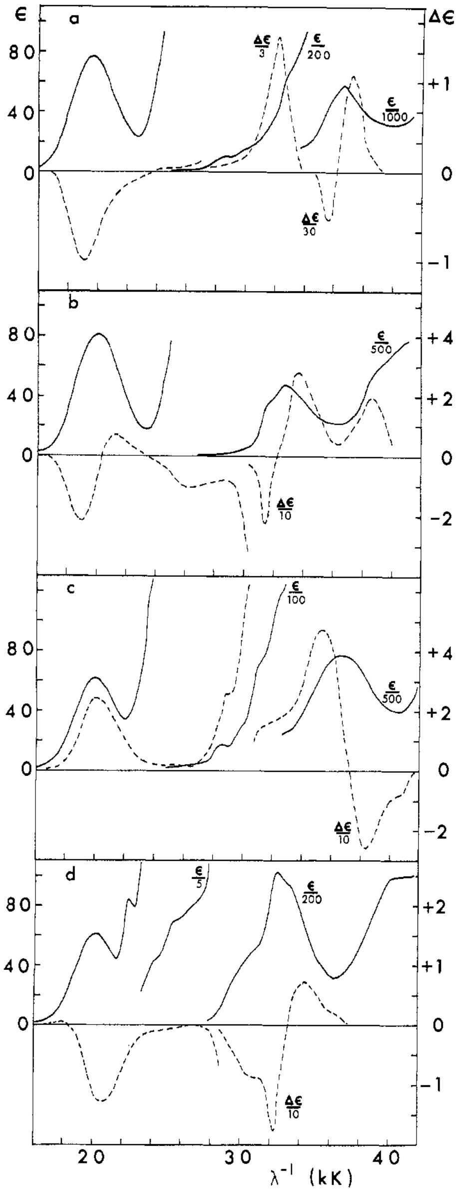

Figure 2.—Absorption (——) and circular dichroism spectra (---) of (a) l-Co(phen)$_2$(ox)$^+$, (b) l-Co(bipy)$_2$(ox)$^+$, (c) d-Cr(phen)$_2$(ox)$^+$, and (d) l-Cr(bipy)$_2$(ox)$^+$ in aqueous solution.

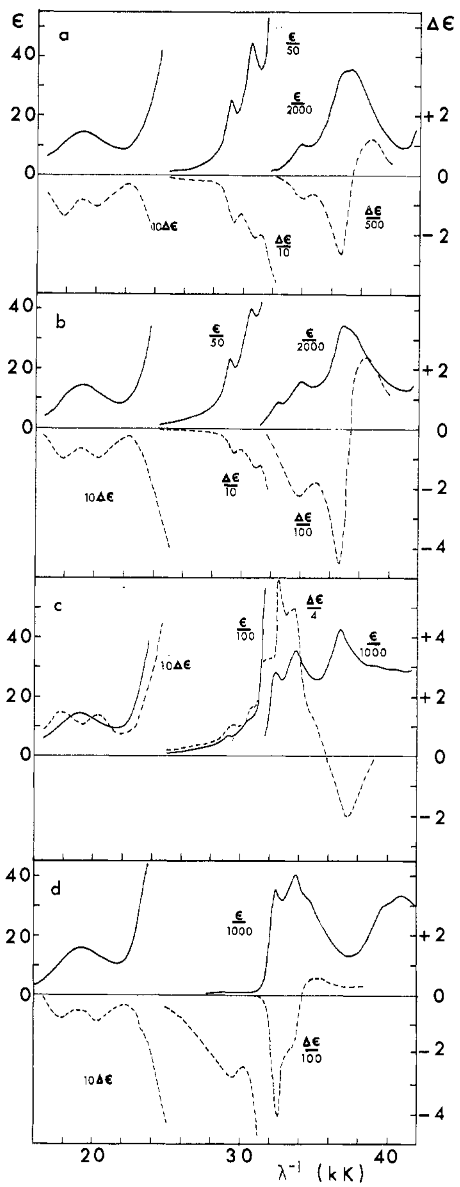

Figure 3.—Absorption (——) and circular dichroism spectra (---) of (a) l-Ni(phen)$_3{}^{2+}$, (b) l-Ni(phen)$_2$(bipy)$^{2+}$, (c) d-Ni(bipy)$_2$(phen)$^{2+}$, and (d) l-Ni(bipy)$_3{}^{2+}$ in alcoholic solution at about 0°.

complexes at low temperatures in solutions of ethyl alcohol cooled with liquid nitrogen with the intention of sharpening the spectra. However, it was found that these spectra were comparable with those taken in water at room temperature, so the latter were used.

Theory

Energy Levels of the Bis and Tris Complexes.—The simplest approach to this problem is to neglect the metal ion and consider the effect of the electrostatic interaction between the ligands by a Coulombic term V. The total Hamiltonian for a tris complex is

$$H = H_A + H_B + H_C + V_{AB} + V_{BC} + V_{AC}$$

where H_A, H_B, and H_C represent the ligand Hamiltonians in the absence of the interaction. If the following functions define the ground and excited states: $\phi = \psi_A\psi_B\psi_C$ (ground state), $\phi_A = \psi_A'\psi_B\psi_C$, $\phi_B = \psi_A\psi_B'\psi_C$, and $\phi_C = \psi_A\psi_B\psi_C'$, where the primed functions denote electronically excited molecules, then the excitation energies are given by

$$\Delta E(A_2) = w' - w + 2(V' - V) + 2\Sigma$$
$$\Delta E(E) = w' - w + 2(V' - V) - \Sigma$$

In these equations w and w' refer to the electronic energies of the ground and excited states, respectively, and the remaining terms are defined by

$$V' = \psi_A'\psi_A'V_{AB}\psi_B\psi_B \, d\tau$$
$$V = \psi_A\psi_A V_{AB}\psi_B\psi_B \, d\tau$$
$$\Sigma = \psi_A'\psi_A V_{AB}\psi_B'\psi_B \, d\tau$$

The A_2 and E states of the tris complex are therefore separated by an amount equal to 3Σ, where Σ is the excitation resonance energy. In principle, the excitation energies can be calculated theoretically by evalua-

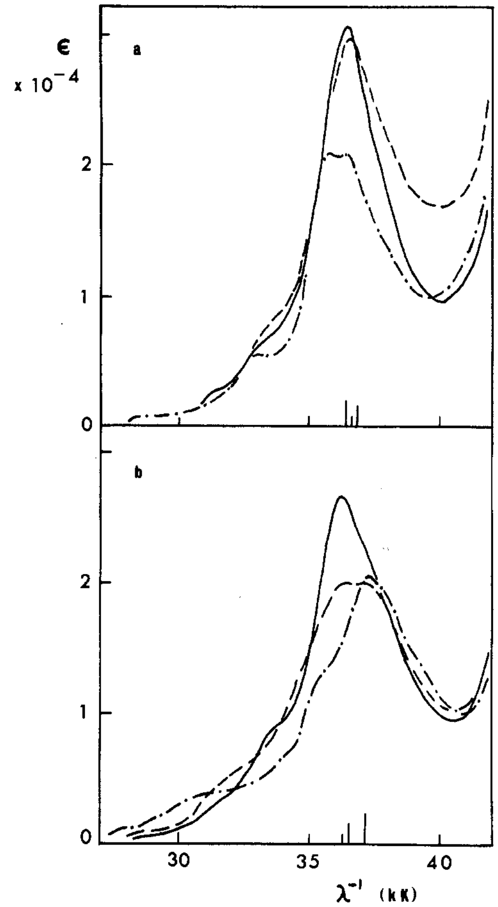

Figure 4.—Ultraviolet absorption spectra per mole of 1,10-phenanthroline for (a) *dl*-$\mathrm{Co(en)_2(phen)^{3+}}$ (——), *l*-$\mathrm{Co(phen)_2(ox)^{+}}$ (---), and *d*-$\mathrm{Co(phen)_3^{3+}}$ (-·-·) and (b) *dl*-$\mathrm{Cr(ox)_2(phen)^{-}}$ (——), *d*-$\mathrm{Cr(phen)_2(ox)^{+}}$ (---), and *d*-$\mathrm{Cr(phen)_3^{3+}}$ (-···) in aqueous solution.

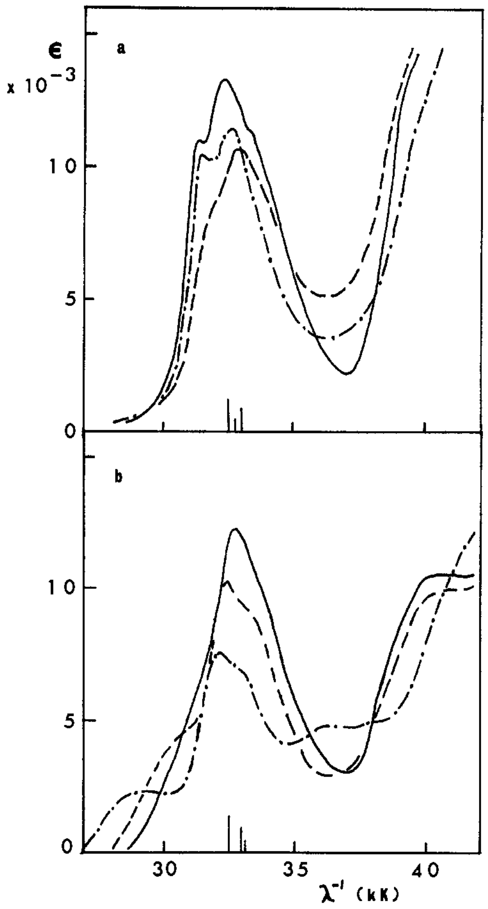

Figure 5.—Ultraviolet absorption spectra per mole of 2,2′-bipyridine for (a) *dl*-$\mathrm{Co(en)_2(bipy)^{3+}}$ (——), *l*-$\mathrm{Co(bipy)_2(ox)^{+}}$ (---), and *l*-$\mathrm{Co(bipy)_3^{3+}}$ (-···) and (b) *dl*-$\mathrm{Cr(ox)_2(bipy)^{-}}$ (——), *l*-$\mathrm{Cr(bipy)_2(ox)^{+}}$ (---), and *dl*-$\mathrm{Cr(bipy)_3^{3+}}$ (-···) in aqueous solution.

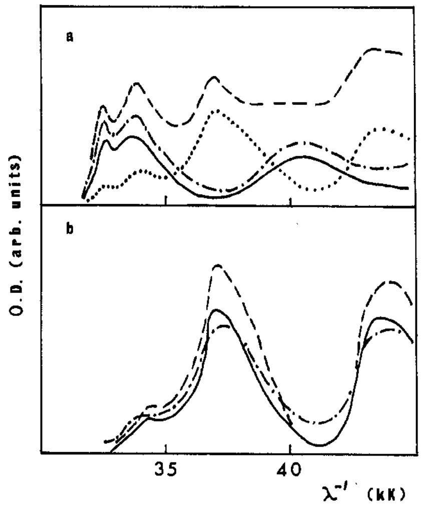

Figure 6.—Ultraviolet absorption spectra with optical density expressed in arbitrary units for (a) *dl*-$\mathrm{Ni(en)_2(bipy)^{2+}}$ (——), *l*-$\mathrm{Ni(phen)_2(bipy)^{2+}}$ (····), *d*-$\mathrm{Ni(bipy)_2(phen)^{2+}}$ (---), and *l*-$\mathrm{Ni(bipy)_3^{2+}}$ (-···), and (b) *dl*-$\mathrm{Ni(en)_2(phen)^{2+}}$ (——), *dl*-$\mathrm{Ni(phen)_2(en)^{2+}}$ (---), and *l*-$\mathrm{Ni(phen)_3^{2+}}$ (-···) in alcoholic solution at 0°.

tion of V', V, and Σ. However, this would require accurate wave functions for the ligands and an accurate form for V_{AB}. Generally this is not done and instead an approximate form for V_{AB} is used. Under certain conditions (see, for example, ref 13) V_{AB} can be expanded as a point multipole series, of which only the first term is retained in order to evaluate Σ. This is the dipole–dipole approximation, and using it Σ is given by

$$\Sigma(\mathrm{dd}) = -e^2[3(\mathbf{p}_A\mathbf{R})(\mathbf{p}_B\mathbf{R}) + R^2(\mathbf{p}_A\mathbf{p}_B)]/R^5$$

where $\mathbf{p}_A$ and $\mathbf{p}_B$ are transition dipoles located at the molecular centers and R is the separation between them.

Specifically for phenanthroline and bipyridine ligands and a long-axis-polarized absorption transition, Σ(dd) has the value $3p^2/(4R^3)$. It is therefore a consequence of the dipole–dipole form of V_{AB} and the geometry of the octahedral complex that the A_2 state must lie at a higher energy than the E state. This approach has been followed by Mason and his coworkers.[5,6,8]

More recently, Mason and Norman[9] have calculated the resonance splittings by using Hückel molecular orbitals to estimate the dipole–dipole energies. How-

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(13) D. P. Craig and T. Thirunamachandran, *Proc. Phys. Soc.* (London), **84**, 781 (1964).

ever, as has been pointed out by Murrell and Tanaka,[14] this type of calculation overestimates by at least a factor of 5 the resonance energies. The second-order interactions (between phenanthroline and bipyridine) are then too large by an order of magnitude. The large interaction energies which are assigned from the circular dichroism spectra on the basis of the calculated energies should therefore be viewed with suspicion.

Whereas the value of Σ has been estimated by the above approximate procedure, the integrals V' and V are usually neglected because they produce the same energy shift in both A_2 and E excitation energies. There are, however, good reasons for neglecting the $V' - V$ term explicitly when relating the levels of the tris complex to that of the mono complex. This term measures the change in the dispersion energy of interaction between two ligands after one has been electronically excited. The term is therefore of the same type which gives rise to a decrease of excitation energy on going from the vapor to the condensed phase, and it is therefore just one of a large number of similar terms if a more general Hamiltonian, which includes Coulombic interactions between the ligands and solvent molecules, is considered. If the energy levels of the solvated "trimer" are to be compared with the energy levels of the solvated "monomer" then $V' - V$ can be absorbed into $w' - w$. This procedure is substantiated by analyses of the spectra of dimers of aromatic hydrocarbons.[15–17]

The same procedure can be applied to the bis complexes, MX_2Y, in which the z axis bisects the Y bidentate ligand. The resulting energy levels are

$$\Delta E(\mathrm{B}) = w' - w + V' - V + \Sigma$$
$$\Delta E(\mathrm{A}) = w' - w + V' - V - \Sigma$$

with V', V, and Σ defined in the same way as for the tris complex. If Σ is approximated by the dipole–dipole term, then the B state must lie at higher energy and this is the assumption used by Bosnich.[7]

A fundamental objection to this simple model is the neglect of the metal ion and covalency. It is now well established,[18] even for ionic crystals such as $KNiF_3$, that σ and π covalencies between a metal ion and its ligands dominate the contributions to the ligand field splitting of the metal d orbitals. Descriptions of the ground and excited states of a metal complex should then be put in the language of molecular orbital theory. Orgel[19] realized this and he has given the symmetry orbitals for π bonding in D_3 complexes. The symmetry orbitals of π type are given in Table II relative to the labeling of Figure 7. The ligand π orbitals are classified as ψ and χ. ψ orbitals are symmetric to the C_2 symmetry axis whereas the χ orbitals are antisymmetric to rotation about this axis. Note that the ψ set spans the A_2 and E representations of D_3, while the χ set and the t_{2g} orbitals span A_1 and E. (The long-axis-polarized transition of the bipyridine ligand corresponds to the orbital jump $\pi(\chi) \rightarrow \pi^*(\psi)$.[19]) There is therefore a splitting of the otherwise triply degenerate ligand π and π^* orbitals which depends on overlap and covalency effects involving the t_{2g}, π, and π^* orbitals. (See Figure 8 for a schematic representation of one possible splitting pattern.) Viewed in this way we can therefore say that the degeneracy of the ligand orbitals is lifted by the trigonal field of the d orbitals. Additional splittings arise from considerations of σ bonding and it can be concluded that the relative energy order of the components of the ψ and χ ligand orbitals is sensitive to the details of σ and π covalencies which might vary from metal ion to metal ion. McCaffery, Mason, and Norman[4] concluded that π covalency is significant but they have apparently assumed that the relative energy order of the components of the ligand π and π^* orbitals is independent of the metal ion.

If the above molecular orbital model is taken further to include explicitly the interaction between the ligand electrons, then there will be additional interactions which will alter the ligand orbital energies. These are analogous to the resonance excitation energies outlined in the first part of this section. It is evident then that within an extended molecular orbital theory the difference between the excitation energies of the A_2 and E components of a ligand transition is given by the sum total of a number of terms which depend on the nature of the metal ion as well as the ligand. It is quite possible that these might cancel and our data suggest that this is so for the nickel complexes we have studied. Certainly there is no compelling reason for neglecting the role of metal–ligand covalency in determining the splitting between the A_2 and E ligand states and we put forward the view here that the relative order should be determined from an analysis of the absorption spectra.

Method Used for Assigning the Absorption Spectra.—The splittings for the tris complexes are determined in the following way. The transition moment of the transition to the A_2 state corresponds to the in-phase addition of the moments of the basis set, while in the transition to the E state they are out of phase. As a result, with the help of three-dimensional geometry, it can be shown that the ${}^1A_1 \rightarrow {}^1A_2$ transition is twice as intense as ${}^1A_1 \rightarrow {}^1E$. However, it is clear from a cursory examination of the spectra that the splitting between the A_2 and E states is small in every case, so that the corresponding bands overlap strongly and an assignment cannot be made by simple inspection of the data. In any case vibronic coupling (treated theoretically by Perrin and Gouterman[20]) alters the band shapes and intensity distributions in a complicated way so that splittings are not easily assigned. The approach used

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[14] J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).
[15] J. Ferguson, *J. Chem. Phys.*, **44**, 2677 (1966).
[16] E. A. Chandross and J. Ferguson, *ibid.*, **45**, 397, 3554 (1966).
[17] E. A. Chandross, J. Ferguson, and E. G. McRae, *ibid.*, **45**, 3546 (1966).
[18] R. E. Watson and A. J. Freeman, *Phys. Rev.*, **134**, A1526 (1964).
[19] L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).
[20] M. H. Perrin and M. Gouterman, *J. Chem. Phys.*, **46**, 1019 (1967).

TABLE II

SYMMETRY ORBITALS FOR D_3 COMPLEXES (π TYPE)

Rep	Metal	Ligand
A_1	$(1/\sqrt{3})(d_{xy} + d_{xz} + d_{yz})$	$(1/\sqrt{3})(\chi_A + \chi_B + \chi_C)$
A_2	......	$(/\sqrt{3})(\psi_A + \psi_B + \psi_C)$
E	$(1/\sqrt{2})(d_{xz} - d_{yz})$ $(1/\sqrt{6})(2d_{xy} - d_{xz} - d_{yz})$	$(1/\sqrt{2})(\psi_B - \psi_C)$; $(1/\sqrt{2})(\chi_B - \chi_C)$ $(1/\sqrt{6})(2\psi_A - \psi_B - \psi_C)$; $(1/\sqrt{6})(2\chi_A - \chi_B - \chi_C)$

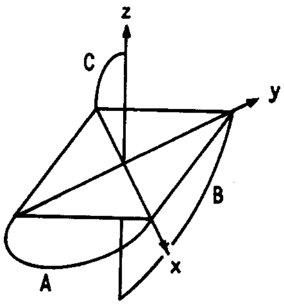

Figure 7.—Orientation of coordinate axes and labeling of ligands in a tris(bidentate) complex (with L configuration).

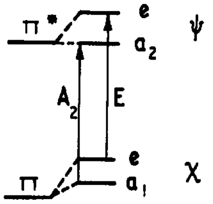

Figure 8.—Schematic representation of one possible splitting pattern for the ligand π and π^* orbitals.

here has been to compare the spectrum of a tris complex with the spectrum of the complex in which two of the ligands are replaced by oxalate or ethylenediamine. The centers of gravity of the $\pi \rightarrow \pi^*$ ligand transitions in the mono and the tris complex spectra are then determined by band area analysis and compared. If the center of gravity of the tris spectrum lies above that of the mono, then it follows that the A_2 state lies above the E state. If it is below, then the A_2 state lies lower in energy.

The assumption behind this procedure follows from our analysis of the energy levels of the tris complex, given in the previous section. It was concluded there that the excitation energies of the A_2 and E components differ from the "monomer" energy because of the combined effects of the trigonal field and excitation resonance interactions. All other energy terms are taken to be equal for the mono and the tris complexes.

Similar arguments can be applied to the case of the bis complex. Here the transition to the B state corresponds to the in-phase addition of transition moments and its intensity is 3 times that of the transition to the A state. The relative order of the two states is then decided by comparison of the centers of gravity of the intensities of the spectra of the mono and the bis complexes.

Rotational Strengths of the Ligand Long-Axis-Polarized Transitions.—The rotational strength of a transition can be expressed as the scalar product of its electric and magnetic dipole moments. The magnetic dipole component of the long-axis-polarized 1,10-phenanthroline and 2,2′-bipyridine transitions comes from the displacement currents associated with the oscillating electric dipole transition moments.[21] The current in one ligand is $\mathbf{j} = (1/c)\delta\mathbf{p}/\delta t$, and for a ligand at a distance R from its center there is a magnetic moment $\mathbf{m} = (1/2c)(\mathbf{R}\delta\mathbf{p} \times \delta\mathbf{t})$. The total moment is obtained by coupling individual moments resulting from the excitations contained in the wave functions for the A_2 and E states for the tris complexes.

For the tris complexes with the D absolute configuration, the total magnetic dipole moment of the in-phase (A_2) component is antiparallel with its electric dipole moment and the rotational strength is therefore negative, whereas the two dipole moments are parallel for the out-of-phase (E) component, and its rotational strength must be positive. For the bis complexes the excitations corresponding to the in-phase (B) and out-of-phase (A) oscillations of the component transition moments have negative and positive rotational strengths, respectively, for the D configuration. For the L configurations the signs are of course reversed.

These clear-cut relations allow the configuration of a resolved bis or tris complex to be determined from a measurement of the circular dichroism provided the relative order of the energies of the in-phase and out-of-phase absorption components can be assigned with certainty.

Discussion

The first point to note from Table I is that the spectra do not show features which are consistent with the dipole–dipole approximation for Σ. The 1,10-phenanthroline complexes of chromium(III) form the only group for which the in-phase components of both the bis and the tris complexes lie at higher energy than the mono complex. The values of Σ which correspond to the observed centers of gravity are 500 cm^{-1} for the bis and 900 cm^{-1} for the tris complex. The first of these is just what is predicted from the term $3p^2/(4R^3)$,

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[21] A. D. McLauchlan and M. A. Ball, *Mol. Phys.*, **8**, 581 (1964).

TABLE III

SPECTROSCOPIC DATA FOR THE d-d TRANSITIONS[a]

Complex	Absorption λ^{-1}, kK	Absorption ϵ	CD λ^{-1}, kK	CD $\Delta\epsilon$	Trans[b]	Abs conf
d-$Cr(phen)_2(ox)^+$	20.00	62.2	20.05	+2.433	E	D
d-$Cr(phen)_3^{3+}$	22.47	364[c]	21.90	+2.520	E?	D?
l-$Cr(bipy)_2(ox)^+$	20.10	61.1	17.92	+0.055	?	
			20.55	−1.274		
l-$Co(phen)_2(ox)^+$	19.70	77.3	19.23	−0.990	E	L
d-$Co(phen)_3^{3+}$	21.98	99.1[d]	20.40	+1.189	?	
l-$Co(bipy)_2(ox)^+$	20.05	81.3	19.05	−2.150	E	L
			21.28	+0.693		
l-$Co(bipy)_3^{3+}$	22.22	71.5	19.90	−0.300	A_2	D
			22.27	+3.050	E	
l-$Ni(phen)_3^{2+}$	19.23	14.3	17.85	−0.136		
			20.00	−0.108		
l-$Ni(phen)_2(bipy)^{2+}$	19.23	14.4	17.86	−0.102		
			20.20	−0.100		
d-$Ni(bipy)_2(phen)^{2+}$	19.23	14.3	17.86	+0.146		
			20.32	+0.140		
l-$Ni(bipy)_3^{2+}$	19.23	15.7	17.92	−0.077		
			20.37	−0.087		

[a] First spin-allowed cubic band for cobalt(III) and chromium(III) complexes and the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ cubic band for the nickel(II) complexes. [b] D_3 representations assigned on the assumptions that the E component dominates for tris complexes and that a transition with this parentage dominates for the *cis*-bis(bidentate) complexes. [c] Very weak shoulder. [d] Shoulder.

but this is taken to be fortuitous and in no way justifies the approximations of the model. The remaining spectra indicate that the ordering of the levels shows no consistent pattern, as we expected from considerations arising out of the molecular orbital analysis. Further, it should be noted that the order of the components for 1,10-phenanthroline complexes need not be the reverse of that for the corresponding 2,2′-bipyridine complexes as proposed by Mason and his coworkers;[4] in the cobalt(III) bis and tris complexes the orders of the in-phase and out-of-phase components are identical.

The absolute configurations of the complexes based on the signs of the Cotton effects of the $\pi \rightarrow \pi^*$ ligand transitions are given in Table I. From this it is seen that *d*-$Co(phen)_3^{3+}$ has the L configuration, enantiomeric to that assigned by Mason and Norman.[8]

The empirical method for the allocation of absolute configurations to tris cobalt(III) and chromium(III) complexes depends on the identification of the E and A_2 components of the first spin-allowed ligand field absorption band. It has been found that the E symmetry transition has a positive and the A_2 a negative Cotton effect for the D configuration.[1,2] The components have previously been assigned by three methods: circular dichroism studies of uniaxial crystals,[22] the relative effect of added salts containing such anions as phosphate, sulfate, and selenite, which is specific for diamine ligands with hydrogen atoms attached to the nitrogen donors and oriented in a specific manner,[23,24] and, finally, the most dominant component being assigned to the E symmetry transition. The last method, which is the one most generally used, is not very sound especially when the measured Cotton effects do not differ markedly or when a circular dichroism band of a neighboring transition significantly overlaps the region of the first ligand field band. Mason and Norman[8] used this method when they applied the empirical method to *d*-$Co(phen)_3^{3+}$. However, there is a large negative circular dichroism band overlapping the region of interest and, therefore, the dominant band directly under the first ligand field band need not necessarily be the $^1A_1$–^1E transition as stipulated by Mason and Norman.[8]

Circular dichroism data for the first spin-allowed ligand field absorption band are tabulated in Table III. Absolute configurations assigned on the basis of the dominance of the E symmetry component, which are also listed, are in agreement with the nonempirical assignments for *l*-$Co(bipy)_3^{3+}$ and *d*-$Cr(phen)_3^{3+}$ although the validity of the assignment for the latter is questionable as the observed Cotton effect under the first ligand field band is superimposed on a much larger band of higher energy.

It has not been possible by the method described here to identify the components of the long-axis-polarized $\pi \rightarrow \pi^*$ ligand absorption band for the nickel(II) complexes. However, it is possible to relate the configurations by comparing the Cotton effects under the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ cubic absorption band. From Table III it would seem that the *d* isomers of $Ni(phen)_3^{2+}$, $Ni(phen)_2(bipy)^{2+}$, and $Ni(bipy)_3^{2+}$ all have the same configuration. According to Mason and his coworkers, *d*-$N(phen)_3^{2+}$ and *l*-$Ni(bipy)_3^{2+}$ have the same absolute configuration contrary to the above conclusion.[4] They based their conclusions on the fact that these isomers form the least soluble antimonyl *d*-tartrate

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(22) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 6, 359 (1963).
(23) S. F. Mason and B. J. Norman, *Chem. Commun.*, 73 (1965).
(24) J. R. Gollogly and C. J. Hawkins, *ibid.*, 689 (1968).

diastereoisomers and have "common physiological specificity." The diastereoisomer solubility criterion would seem to be unsound as the phenanthroline complex crystallizes as (d-Ni(phen)$_3$)(d-SbOtart)$_2 \cdot 7H_2O$ and the bipyridine complex as (l-Ni(bipy)$_3$)$_3$(d-SbOtart)$_4I_2 \cdot 18H_2O$. Further, the relative solubilities of the possible diastereoisomers depend on the concentration of the resolving agent that has been used.[25] In addition, the assignment of relative configurations based on the common physiological specificity of the complexes is not supported by the literature. Although much has been published on the physiological action of 1,10-phenanthroline and 2,2′-bipyridine complexes, the stated comparison was not found.[26]

Although it was not possible with the present circular dichrograph to study the complete $^3T_{1g}$ band, the highest energy component centered at about 13 kK for the four nickel complexes was found to be positive for the l isomers. By comparison with the circular dichroism of L-tris(l-*trans*-1,2-diaminocyclohexane)-nickel(II) for both this band and the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ band,[27] it can be concluded that the l isomers have the L configuration.

For *cis*-bis(bidentate) complexes, one of the components with E trigonal parentage generally seems to dominate the circular dichroism spectra in the vicinity of the first ligand field band.[28] The absolute configurations assigned on this basis agree with those from the nonempirical method except for l-Cr(bipy)$_2$(ox)$^+$, which also has an overlapping Cotton effect from a neighboring transition.

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[25] See, for example, A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor Ed., Academic Press, New York, N. Y., 1964, pp 218–220.

[26] For a comprehensive review of the subject see A. Shulman and F. P. Dwyer, ref 25, pp 383–439.

[27] R. S. Treptow, *Inorg. Chem.*, **7**, 1229 (1968).

[28] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT 06268

Polysulfide Chelates. II. Desulfuration of PtS_{15}^{2-} and the Synthesis of PtS_{10}^{2-} [1a,b]

BY ADRIENNE E. WICKENDEN[1c] AND RONALD A. KRAUSE

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A reproducible method for obtaining a high yield of $(NH_4)_2PtS_{15}$ from a polysulfide solution is described. One ligand reaction, the attack of polysulfide chelate rings by cyanide ion, has been investigated in detail. The over-all stoichiometry of this reaction has been shown to be: $PtS_{15}^{2-} + 17CN^- \rightarrow Pt(CN)_4^{2-} + 13SCN^- + 2S^{2-}$. Early in the reaction a new polysulfide chelate, PtS_{10}^{2-}, may be isolated as a tetrapropylammonium salt. This compound has been characterized and compared with $(NH_4)_2PtS_{15}$. The new complex consists of planar platinum(II) surrounded by two pentasulfide chelating ligands. During the course of the cyanide reaction a novel electron transfer occurs reducing platinum(IV) to platinum(II).

Introduction

Polysulfides should be capable of forming a novel class of coordination compounds, complexes in which each chelate ring consists of only one metal ion and several sulfurs. We have reported a method[1a] whereby the polysulfide has been constructed about the metal ion *via* the template effect. One should also be able to utilize polysulfide ions to synthesize such complexes. Several compounds have been reported which probably contain chelating polysulfides but have not been recognized as such. Most recently Köpf, Block, and Schmidt[2] have demonstrated that the compound which they synthesized, $Ti(C_5H_5)_2S_5$, does contain a polysulfide chelate ring.

One of the most interesting polysulfide complexes, $(NH_4)_2PtS_{15}$, was isolated by Hofmann and Höchtlen in 1903.[3] They were aware of the fact that S_5^{2-} groups were probably present, but they did not propose a structure for the compound. Recently, Jones and Katz[4] reported the crystal structure of $(NH_4)_2PtS_{15}$ and confirmed that it does indeed contain pentasulfide chelate rings about platinum(IV).

We are currently investigating the chemistry of this compound in some detail. One aspect of considerable

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[1] (a) For Part I see N. B. Egen and R. A. Krause, *J. Inorg. Nucl. Chem.*, **31**, 127 (1969). (b) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968. (c) From a dissertation submitted to the Graduate School of the University of Connecticut by A. E. W. in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, **101**, 272 (1968).

[3] K. A. Hofmann and F. Höchtlen, *ibid.*, **36**, 3090 (1903).

[4] P. E. Jones and L. Katz, *Chem. Commun.*, 842 (1967).