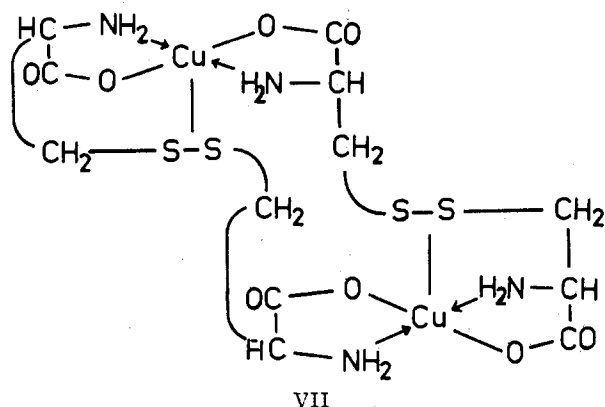


the structure VII.



In this structure, each copper forms part of three five-membered rings while at the same time both coppers are linked in a multi-membered ring. The blue, finely crystalline complex precipitated from neutral solutions of cystine containing copper(II) ion is believed to be VII, which is the form in which most of the copper is

present in solution under the experimental conditions; this species would be expected to be only sparingly soluble because of its non-ionic character. Chemical analysis is consistent with this structure, but its molecular weight could not be determined because of insolubility. The magnetic moment of 1.91, determined by the Gouy method, is identical with that for the corresponding DAS complex,<sup>6</sup> again indicating the absence of Cu-Cu  $\delta$ -bonding. Leybold atomic models confirm that structure VII is possible, but provide no information about the stereochemistry of the bond between the copper and the -S-S- groups. Appreciable vertical movement can occur for the -S-S- group when it is located above a copper atom, and sufficient lateral displacement is possible that bonding could be through either sulfur atom or through a  $\pi$ -bond involving one of their shared orbitals.

**Acknowledgments.**—The authors thank Miss Elizabeth Reid for the computer program and operation and Dr. N. Gill for use of the magnetic balance.

CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES  
OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND

## Some Transition Metal Complexes of Ethylenethiourea. I. Cobalt(II)<sup>1</sup>

BY RICHARD L. CARLIN AND SMITH L. HOLT, JR.

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A series of compounds involving ethylenethiourea coordinated to the cobalt ion in the halides and perchlorate has been prepared and characterized. Tetrahedral stereochemistry is found in each case. This conclusion is based on the careful measurement and analysis of the visible spectra and magnetic susceptibilities. The complex derived from cobalt acetate and ethylenethiourea is probably octahedral. Ethylenethiourea occurs at the very low end of the nephelauxetic series.

Cotton, Goodgame, and Goodgame<sup>2</sup> have shown how the stereochemistry of cobalt(II) may be characterized by a careful study of the electronic spectra and paramagnetic susceptibilities of a series of similar compounds. Valuable data are obtained for the electronic parameters of the tetrahedral metal ion, while useful information is also gained concerning the ligands. Thus, the order of the various ligands in the spectrochemical and nephelauxetic series has been obtained, as well as information concerning the variation in spin-orbit coupling constants in the complexes. Knowledge concerning the solvent effects on the spectra may also be obtained in this manner.

Little information, however, has been included in previous studies of the first row metal ions on sulfur as a donor atom. Sulfur is frequently less effective than its congener, oxygen, in its ability to function as a donor to first row metal ions. This is, of course, only a relative matter; witness the many sulfide precipitates,

as well as the much greater stability of compounds formed by thioethers compared to ethers.

Nardelli and co-workers<sup>3</sup> have recently prepared several complexes of ethylenethiourea (2-imidazolidinethione, etu) with the chlorides of iron(II), nickel, and cobalt. Their work consisted of preparation, analysis, and characterization by X-ray crystallographic techniques; their results showed that sulfur was the donor atom. Neither the spectra nor the magnetic susceptibilities of any of these compounds were reported. Pursuant to our interest in sulfur as a donor atom, we have prepared the same complexes as well as those resulting from the use of other salts of the metals and have measured the electronic parameters characterizing ethylenethiourea as a ligand. In this paper we report our work on cobalt(II) and we shall report later on the complexes of other metal ions.

### Experimental<sup>4</sup>

The earlier report<sup>3</sup> of the preparation of  $\text{CoCl}_2 \cdot 2\text{etu}$  involved

(3) M. Nardelli, I. Chierici, and A. Braibanti, *Gazz. chim. ital.*, **88**, 37 (1958).

(4) Microanalyses are by Schwarzkopf Microanalytical Laboratory.

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961), and earlier papers.

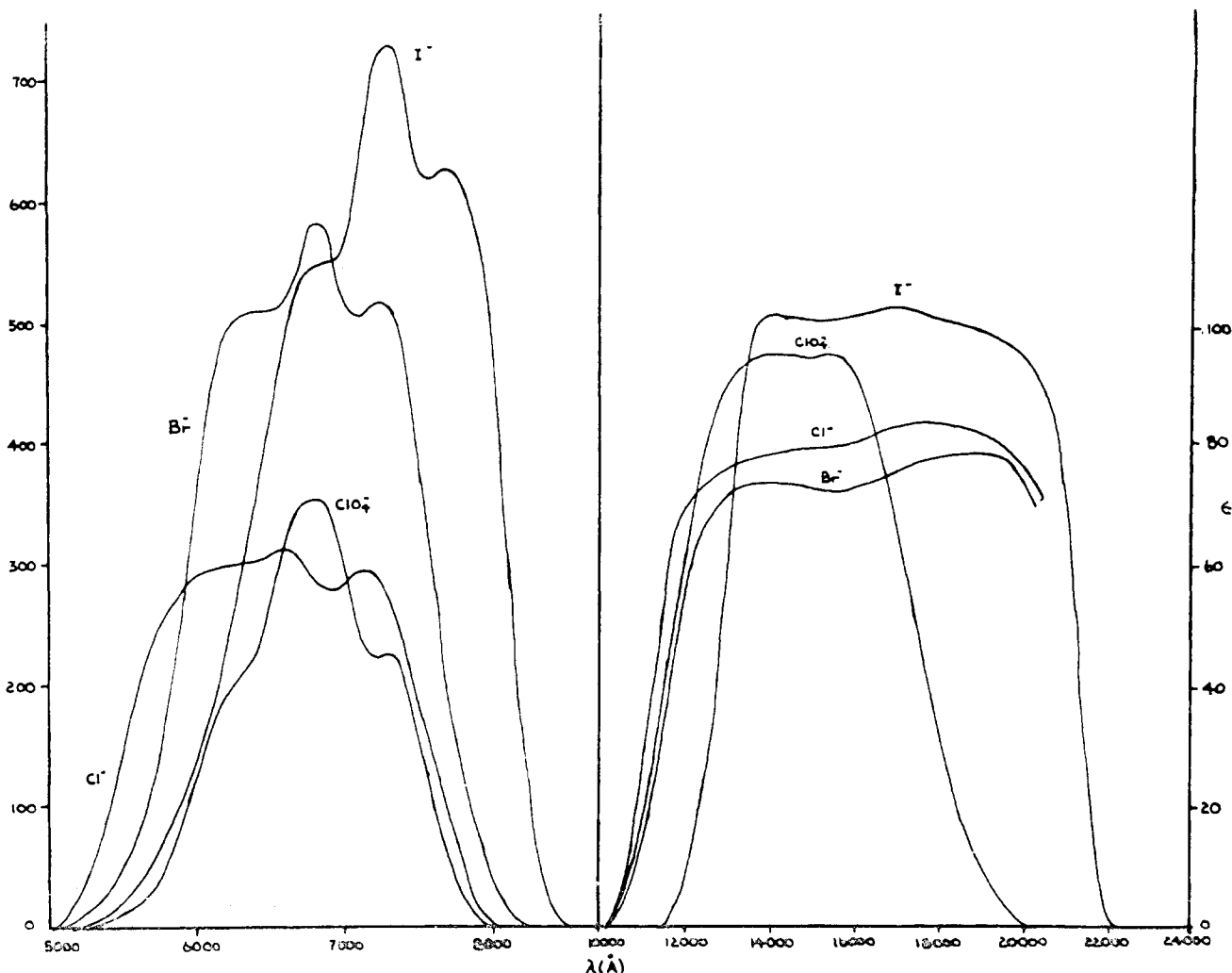


Fig. 1.—Spectra of the tetrahedral complexes in acetone

the slow evaporation at ambient temperature of a solution of 10  $\text{CoCl}_2$  to 1  $\text{etu}$  in aqueous alcohol. We have been unable to repeat the preparation by this method.

**Reagents.**—All metal salts were reagent grade and were used without further purification. Ethylenethiourea was obtained commercially (K and K) and was purified by recrystallization from ethanol.

**Dichlorobis-(ethylenethiourea)-cobalt(II).**—A hot ethanolic solution of anhydrous cobalt chloride is mixed with a similar solution of ethylenethiourea in approximately a 1:2 mole ratio. Upon cooling, azure-blue crystals of the compound appear which were recrystallized carefully from hot ethanol and dried *in vacuo* at  $100^\circ$ .

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_4\text{S}_2\text{CoCl}_2$ : C, 21.55; H, 3.59; N, 16.75. Found: C, 21.84; H, 3.55; N, 16.40.

**Dibromobis-(ethylenethiourea)-cobalt(II).**—Azure-blue to blue-green crystals were obtained by the same procedure as for the chloride.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_4\text{S}_2\text{CoBr}_2$ : C, 17.01; H, 2.84; N, 13.25. Found: C, 17.30; H, 3.23; N, 12.80.

**Diiodobis-(ethylenethiourea)-cobalt(II).**—Grass green crystals were obtained by the same method as above.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_4\text{S}_2\text{CoI}_2$ : C, 13.94; H, 2.33; N, 10.82. Found: C, 13.64; H, 2.05; N, 10.80.

**Diacetabis-(ethylenethiourea)-cobalt(II).**— $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (14 g.) is dissolved in cold absolute alcohol and added to a hot solution of 14 g. of ethylenethiourea in ethanol. On standing purple crystals precipitate which are recrystallized from hot alcohol (some decomposition was noticed) and dried at  $100^\circ$  *in vacuo*.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{18}\text{N}_4\text{S}_2\text{CoO}_4$ : C, 31.49; H, 4.72; N, 14.69. Found: C, 31.70; H, 4.96; N, 14.36.

**Tetrakis-(ethylenethiourea)-cobalt(II) Perchlorate.**—A hot solution of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in alcohol is added to a similar solution of ethylenethiourea in a 2:1 mole ratio. Excess of salt is required in order to prevent the coprecipitation of ethylenethiourea with the compound. Upon standing blue crystals of the new compound precipitate and are recrystallized from hot ethanol. Some decomposition of the complex to free ethylenethiourea accompanies recrystallization. The crystals are dried *in vacuo* at  $100^\circ$ .

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{24}\text{N}_8\text{S}_4\text{CoCl}_2\text{O}_8$ : C, 21.70; H, 3.62; N, 16.85. Found: C, 22.24; H, 4.06; N, 17.53.

**Spectral Measurements.**—A Cary Model 14 recording spectrophotometer was used for all measurements. Spectra of the complexes in the visible region were taken in solution and are shown in Fig. 1 and 2. These spectra were checked and extended to the infrared region by use of NaCl pellets. All spectra were also recorded on the reflectance attachment for the Cary,  $\text{MgCO}_3$  being the standard. Good agreement was obtained between pellet and reflectance spectra. Spectra on Nujol mulls were also found to be comparable to the reflectance spectra.

**Magnetic Measurements.**—These were made with a Gouy balance of standard design. The calibrants were Mohr's salt and  $\text{HgCo}(\text{NCS})_4$ . A standard double-walled dewar served for the low temperature measurements.

**Conductivity Measurements.**—These were made with a capacitance-conductance bridge of the Cole-Gross type and a conventional cell, previously calibrated with an aqueous solution of potassium chloride.

$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{etu}$  is insoluble and thus no conductance measurements could be made. Replicate measurements were made on all of the other complexes on solutions  $10^{-3}$ – $10^{-4}$  M. Results reported in Table I refer in each case to the most dilute solution measured.

### Results

The colors of the complexes suggested to us that they were probably all of tetrahedral stereochemistry. The data we report here confirm the hypothesis, with the exception that the acetato complex appears to be octahedral.

The conductivity data in Table I show that all of the halides are essentially non-electrolytes in ionizing solvents. This is in accord with their formulation as  $[\text{Co}(\text{etu})_2\text{X}_2]$ . The measurements show that some solvolysis does occur, however. This suggests the probable formation, at least for the iodide, of the  $[\text{Co}(\text{etu})_2\text{X}(\text{solvent})]^+$  ion. This result agrees with the spectral measurements reported in a subsequent section.

TABLE I  
ELECTROLYTIC CONDUCTIVITIES AT 24°

Compound	Solvent	Molar conductance, ohms <sup>-1</sup>
KI	Acetone	146
$[\text{Co}(\text{etu})_2\text{Cl}_2]$	Acetone	6.7
$[\text{Co}(\text{etu})_2\text{Br}_2]$	Acetone	7.5
$[\text{Co}(\text{etu})_2\text{I}_2]$	Acetone	26.1
$[\text{Co}(\text{etu})_2\text{Br}_2]$	$\text{CH}_3\text{NO}_2$	4.1
$[\text{Co}(\text{etu})_4](\text{ClO}_4)_2$	$\text{CH}_3\text{NO}_2$	190

The magnetic susceptibility of the chloride complex is reported here for the first time, along with the measurements on the four new compounds. The measurements have been made at three temperatures (80–300°K.) on several different samples of each compound. These susceptibility values then were corrected for diamagnetism and temperature-independent paramagnetism (T.I.P.)<sup>2</sup> to provide the fully corrected molar susceptibilities,  $\chi_M^{\text{corr}}$ , which are listed, together with the corrections, in Table II. Reciprocals of these corrected

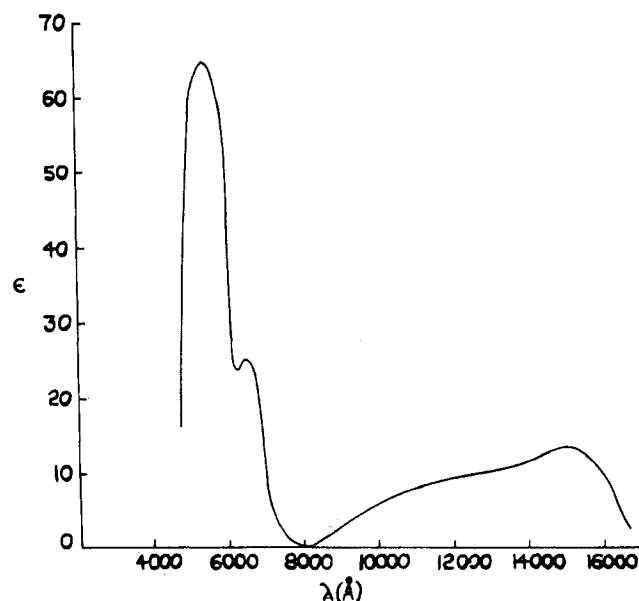


Fig. 2.—Spectrum of the acetato complex in glacial acetic acid.

molar susceptibilities were plotted against temperature and, from the resulting straight lines, the magnitudes of  $\mu$  and  $\theta$  were obtained. The T.I.P. corrections were calculated from the  $Dq$  values in Table IV taking the  $Dq$  value obtained in the NaCl phase, using the relation<sup>2</sup> T.I.P. =  $2.09/10Dq$ .

TABLE II  
MAGNETIC SUSCEPTIBILITY MEASUREMENTS AT 295.5°K.

Compound	Dia. corr. $\times 10^6$	T.I.P. $\times 10^6$	$\chi_M^{\text{corr.}} \times 10^6$ , c.g.s.u.	$\mu$ , B.M.	$\theta$ , °K.
$[\text{Co}(\text{etu})_2\text{Cl}_2]$	-173	620	8295	4.51	-9
$[\text{Co}(\text{etu})_2\text{Br}_2]$	-194	630	8431	4.54	-7
$[\text{Co}(\text{etu})_2\text{I}_2]$	-222	650	8485	4.58	-12
$[\text{Co}(\text{etu})_2(\text{CH}_3\text{COO})_2]$	-218	...	8771	4.64	-9
$[\text{Co}(\text{etu})_4](\text{ClO}_4)_2$	-302	550	9139	4.73	-8

A summary of the spectral data collected in this work is presented in Table III, and the values chosen for the energies of  $\nu_2$  and  $\nu_3$  together with the values of  $Dq$  and  $B'$  derived therefrom are given in Table IV.

TABLE III  
SPECTRAL DATA FOR TETRAHEDRAL COBALT(II) COMPOUNDS<sup>a</sup>

Compound	State	$\nu_3$ , cm. <sup>-1</sup>			$\nu_2$ , cm. <sup>-1</sup>
		15930 (311)	15050 (328)	14150 (287)	
$[\text{Co}(\text{etu})_2\text{Cl}_2]$	Acetone	15930 (311)	15050 (328)	14150 (287)	6350 (87)
	Acetone-etu	16250 (396)	15040 (533)	13980 (474)	
	Nitroethane	16280 (384)	15020 (418)	14040 (334)	
	NaCl	15930	14690	13700	
$[\text{Co}(\text{etu})_2\text{Br}_2]$	Acetone	15490 (516)	14530 (579)	13840 (526)	6230 (79)
	Acetone-etu	15690 (516)	14550 (627)	13700 (659)	
	Nitroethane	15630 (466)	14530 (567)	13700 (584)	
	NaCl	15750	14900	13020	
$[\text{Co}(\text{etu})_2\text{I}_2]$	Acetone	14750 (549)	13870 (708)	13160 (606)	6000 (109)
	Acetone-etu	14900 (570)	13900 (833)	13040 (850)	
	Nitroethane	14875 (766)	13900 (1140)	13040 (1161)	
	NaCl	14820	13790	12770	
$[\text{Co}(\text{etu})_4](\text{ClO}_4)_2$	Acetone	15750 sh	14580 (346)	13870 (215)	6850 (95)
	Acetone-etu	15725 sh	14560	13820	
	Nitroethane	15720 (504)	14600 (726)	13875 (639)	
	NaCl	15780 sh	14510	14090	

<sup>a</sup> Molar extinction coefficients are given in parentheses.

TABLE IV  
SUMMARY OF SPECTRAL ASSIGNMENTS AND DERIVED ELECTRONIC STRUCTURE PARAMETERS  
FOR THE TETRAHEDRAL COBALT(II) COMPLEXES

Compound	State	$\nu_2$ , cm. <sup>-1</sup>	$\nu_3$ , cm. <sup>-1</sup>	$Dq$ , cm. <sup>-1</sup>	$B'$ , cm. <sup>-1</sup>	$\beta$	$\lambda'$ , cm. <sup>-1</sup>
[Co(etu) <sub>2</sub> Cl <sub>2</sub> ]	Acetone	6350	15380	366	717		
	Nitroethane	...	15170	...	...		
	NaCl	5870	14700	339	693	0.71	130
[Co(etu) <sub>2</sub> Br <sub>2</sub> ]	Acetone	6230	14710	360	676		
	Nitroethane	5940	14500	343	676		
	NaCl	5740	14200	332	665	0.69	138
[Co(etu) <sub>2</sub> I <sub>2</sub> ]	Acetone	6000	13840	347	629		
	Nitroethane	5820	13800	336	636		
	NaCl	5560	13510	321	629	0.65	142
[Co(etu) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Acetone	6850	14500	398	627		
	Nitroethane	6500	14600	378	651		
	NaCl	6480	14600	378	651	0.67	204

Selection of single energy values for  $\nu_2$  and  $\nu_3$  is necessarily arbitrary; this problem has been discussed by Cotton, *et al.*,<sup>2</sup> and we follow their procedures. The values of  $Dq$  and  $B'$  were calculated from the energies of  $\nu_2$  and  $\nu_3$  using the equations of Tanabe and Sugano.<sup>5</sup>

### Discussion

**Spectra.**—We take the spectra in sodium chloride pellets as the true spectra of the compounds reported here. These spectra are essentially the same as the reflectance spectra. This gives us confidence that there is no change in the nature of the complexes upon forming the pellet.

This is definitely not true for the compounds in solution, however. The complexes are insoluble in most common solvents, acetone being the only solvent in which the compounds are soluble enough to obtain spectra. We find definite differences between the solution spectra and the true (crystalline sample) spectra. The postulate that the halide compounds are partially solvolyzed is substantiated by the slight but measurable conductivities in ionizing solvents. The perchlorate is of course a typical 1:2 electrolyte.

Spectra in solution are essential in order to determine extinction coefficients. Such data are necessary in order to determine whether or not the absorption intensities fall in a range acceptable<sup>2</sup> for tetrahedral complexes. Addition of excess ethylenethiourea was found to change the spectra slightly, in accord with the postulate of partial solvolysis. While the extinction coefficients reported in Table III may not be correct to better than  $\pm 10\%$ , they fall within a range acceptable for tetrahedral Co(II).

Previous work on the spectrum of cobalt(II) in a field of four sulfur atoms is limited to studies on the ion in tetrahedral sites in CdS<sup>6,7</sup> and ZnS.<sup>7</sup> The preparation of the tetrahedral compound [Co(etu)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> allows us to compare the spectral parameters for the two sulfur donors, sulfide and ethylenethiourea. This is done in Table V, where it can be seen that the spectra, excluding the effects of spin-orbit coupling and low symmetry fields, are similar for the three compounds

containing CoS<sub>4</sub> tetrahedra. These data indicate that ethylenethiourea is higher in the spectrochemical series than sulfide. An even higher value of  $Dq$  (about 400 cm.<sup>-1</sup>) is obtained for the perchlorate compound if the analysis is based on the solution spectra.

The spectrum of the perchlorate compound also

TABLE V  
SPECTRA OF CoS<sub>4</sub> TETRAHEDRA

	$Dq$ , cm. <sup>-1</sup>	$B'$ , cm. <sup>-1</sup>
CdS:Co <sup>++a</sup>	330	610
ZnS:Co <sup>++a</sup>	375	610
CdS:Co <sup>++b</sup>	316	664
[Co(etu) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	378	651

<sup>a</sup> Reference 7, 77°K. <sup>b</sup> Reference 6, 78°K. <sup>c</sup> This work, room temperature, mean values.

allows the positioning of ethylenethiourea in the extensive spectrochemical and nephelauxetic series established by Cotton.<sup>2</sup> Ethylenethiourea lies between azide and triphenylphosphine oxide in the spectrochemical series. It seems impossible to give a rationale for the positions of the ligands in this series. Sulfur is the donor atom<sup>8</sup> in dichlorotetrakis-(thiourea)-nickel(II) as well as in other thiourea complexes studied by Nardelli, and we believe it is also the donor atom in the ethylenethiourea complexes.

On the other hand, the  $B'$  value of [Co(etu)<sub>4</sub>]<sup>2+</sup> is of the order of 66% of the free ion value, which suggests that there is appreciable orbital overlap. This is to be expected, for sulfur is a large, polarizable atom. Again, comparing these data with those of Cotton and co-workers<sup>2</sup> the position of the  $\beta$ -value for ethylenethiourea is at the low end of the nephelauxetic series, approximately in the same position as iodide.

**The Average Ligand Field Approximation.**—This approximation deals with a complex as though it contained identical ligands whose properties will be numerical averages of those of the actual ligands. The availability of reliable  $Dq$  and  $B'$  values for [CoX<sub>4</sub>]<sup>2-</sup> species<sup>2</sup> coupled with our data for the [Co(etu)<sub>4</sub>]<sup>2+</sup> ion gives the necessary information for the calculation of the average ligand field parameters for the [Co(etu)<sub>2</sub>X<sub>2</sub>]

(5) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(6) R. Pappalardo and R. E. Dietz, *Phys. Rev.*, **123**, 1188 (1961).

(7) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(8) L. Cavalca, M. Nardelli, and A. Braibanti, *Gazz. chim. Ital.*, **86**, 942 (1956); M. R. Truter, Proc. 7th Intern. Conf. on Coordination Chemistry, Stockholm, June, 1962.

species. The results of these calculations may be found in Table VI, where it will be seen that the approximation works fairly well.

TABLE VI  
COMPARISON OF OBSERVED AND CALCULATED AVERAGE LIGAND  
FIELDS IN  $[\text{Co}(\text{etu})_2\text{X}_2]$  COMPLEXES

X	Observed		Calculated	
	$Dq$ , cm. <sup>-1</sup>	$B'$ , cm. <sup>-1</sup>	$Dq$ , cm. <sup>-1</sup>	$B'$ , cm. <sup>-1</sup>
Cl	339	693	339-353	671-691
Br	332	665	329-335	661-686
I	321	629	319-324	646-671

**Magnetic Results.**—The magnetic susceptibilities of the complexes fall in the range<sup>2</sup> acceptable for tetrahedral cobalt(II). One of the interesting features of these data is the small variation in the magnetic moment between the various halide compounds. The spectrochemical series requires that the moment decrease in the order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$  yet we find no significant variation, within experimental error. This is probably an indication that the sulfur ligand predominates in its effect on the metal ion due to its higher position in the spectrochemical series. Also, the splittings in the spectral bands are too large to be due to spin-orbit coupling alone, and low symmetry fields contributing to this splitting probably contribute as well to the magnetic moments.

**Spin-Orbit Coupling Constants.**—A most important result of the combined spectral and magnetic study reported here are the  $\lambda'$  values, that is, the effective values of the spin-orbit coupling constants for the Co(II) ion in the complexes. Owen<sup>9</sup> and Dunn<sup>10</sup> have discussed possible reasons why the  $\lambda'$  values in complexes appear generally to be lower than the  $\lambda$  values in the free ion. Orbital overlap resulting in delocalization of the d-electrons has been suggested.

As shown in the bottom row of Table IV,  $\lambda'$  values in all of the tetrahedral Co(II) complexes which have been prepared are 70 to 80% of the free ion value (178 cm.<sup>-1</sup>). The surprising feature is that there is an *increase* in  $\lambda'$

over the free ion value for the perchlorate compound. This is physically unreasonable and we have no ready explanation for this unusual result. The position of ethylenethiourea in the nephelauxetic series (derived from the spectra) suggests a reasonable degree of delocalization.

**The Acetato Compound.**—We have not yet discussed this brilliant purple compound. As may be noticed upon comparison of Fig. 1 and 2, the spectrum of  $[\text{Co}(\text{etu})_2(\text{CH}_3\text{COO})_2]$  is substantially different from the spectra of the other complexes. The spectrum is not typical of tetrahedral cobalt(II); indeed, it is more typical of octahedrally coordinated cobalt(II). The spectrum of the compound in glacial acetic acid is characterized by extinction coefficients in the range 20-60, which lends credence to this supposition. The magnetic susceptibility (corrected) of 4.64 B.M. at 295.5°K. is just below the range expected for octahedral coordination.

The spectrum (Fig. 2) may be assigned<sup>11</sup> for octahedral cobalt(II) as  $\nu_1 = 7350$ ,  $\nu_2 = 14350$ , and  $\nu_3 = 18020$  cm.<sup>-1</sup>. This leads to a value of  $Dq \approx 850-900$  cm.<sup>-1</sup>, which is in the proper range. This value is of course only approximate, for no allowance has been made for the tetragonal component of the ligand field. An absurd value of  $Dq$  is obtained if the spectrum is analyzed in terms of tetrahedral cobalt.

In view of these considerations it would appear that the acetate ligand is bidentate. The compound is soluble without change only in glacial acetic acid. This insolubility suggests that the compound may be a polymer with bridging acetate groups. On the other hand, the two oxygens of the acetate group may both be bound, equivalently or inequivalently, about the central ion. This appears to be the case for the nitrate ligand in  $\text{Co}[\text{OP}(\text{CH}_3)_2](\text{NO}_3)_2$ .<sup>12</sup>

**Acknowledgment.**—We thank George Vidulich for helping with the conductivity measurements. We are grateful to the National Science Foundation for the financial support of this research.

(11) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955). A 15% lowering of the free ion value for  $E$  (<sup>4</sup>P) was assumed.

(12) F. A. Cotton, private communication

(9) J. Owen, *Proc. Roy. Soc. (London)*, **A227**, 183 (1955).

(10) T. M. Dunn, *J. Chem. Soc.*, 623 (1959).