

displacements from  $\text{CF}_2\text{O}$  frequencies, but the more stable structure gave shifts up to  $30\text{ cm}^{-1}$ , which suggests that the latter complex is at least as strong as similar hydrogen-bonded complexes.

**Acknowledgment.** The authors gratefully acknowledge National Science Foundation support for this research, S. R. Davis for assistance with the figures, and C. Trindle for helpful discussions.

**Note Added in Proof.** Complementary mercury arc photolysis experiments have been done with  $\text{Ar/O}_2/\text{CF}_3\text{I}$  matrix samples at 4 K.

These studies gave similar product spectra including perturbed  $\text{OCF}_2$  species, group 3 and group 6 absorptions.<sup>29</sup>

**Registry No.** 2, 56407-83-1; 3, 97551-33-2;  $\text{CF}_3\text{I}$ , 2314-97-8;  $\text{O}_3$ , 10028-15-6;  $^{18}\text{O}_3$ , 21424-26-0;  $^{16,18}\text{O}_3$ , 97551-32-1;  $\text{CF}_2\text{O}$ , 353-50-4; IF, 13873-84-2; Ar, 7440-37-1.

(29) Clemitshaw, K. C.; Sodeau, J. R., paper presented at the 5th International Conference on Spectroscopy of Matrix-Isolated Species, Fontevraud, France, 1985.

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## Circular Dichroism of (Ethylenediaminetetrapropionato)rhodate(III) Ion

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Received August 13, 1984

The ethylenediaminetetrapropionate ion (edtp) is sexidentate in the complex  $[\text{Rh}(\text{edtp})]^-$ . The infrared, electronic absorption, and circular dichroism spectra are reported. The  $\Lambda$  configuration is assigned to the (+)<sub>D</sub> enantiomer by comparison of the CD spectrum with those of Rh(III) edta-type complexes for which absolute configurations are known from X-ray crystallography. Although the electronic absorption intensities are not large for  $[\text{Rh}(\text{edtp})]^-$ , the CD intensities are unexpectedly great in comparison to those of other edta-type complexes of Rh(III).

### Introduction

The structure of the  $[\text{Co}(\text{edta})]^-$  complex<sup>1</sup> shows notable departures from regular octahedral coordination, indicating that the chelate rings are strained. The two glycinate rings (designated as G rings) lying in the plane of the diamine ring are considerably more strained than the out-of-plane glycinate rings (designated as R rings). The larger Cr(III)<sup>2-4</sup> and Rh(III)<sup>3,5</sup> metal ions tend not to form sexidentate edta complexes because of greater ring strain.

The 1,3-pdta,<sup>6</sup> SS-edds,<sup>7-10</sup> and eddda<sup>11,12</sup> ligands (1,3-pdta = 1,3-propanediaminetetraacetate ion; SS-edds = (SS)-ethylenediamine-*N,N'*-disuccinate ion; eddda = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) form six-membered chains when coordinated, and the formation of their sexidentate Rh(III) complexes can be attributed to the relief of strain of chelate rings. Such complexes containing the ligand with mixed (five- and six-membered) rings are of interest in the study of the influence of chelate ring size and their arrangement about a central metal ion and other factors on optical activity.

The sexidentate Rh(III) complexes with eddda,<sup>13,14</sup> SS-edds,<sup>7,14</sup> and 1,3-pdta<sup>15</sup> have been prepared, and their CD spectra were studied. In this paper the edtp ligand (edtp = ethylenediaminetetrapropionate ion), in which four carboxylate groups are lengthened with respect to the edta ligand, has been used in the preparation and resolution of the corresponding sexidentate Rh(III) complex. The IR, electronic absorption, and CD spectra of the complex are reported.

### Experimental Section

All reagent-grade chemicals and solvents were obtained commercially and used without further purification.

Optical isomers are identified by the sign of the optical rotation at a specified wavelength,  $[\alpha]_{\lambda}$  or  $(-)\alpha_{\lambda}$ . The chirality is designated as  $\Delta$  or  $\Lambda$  assigned according to ref 16.

**Preparation of Ethylenediaminetetrapropionic Acid,  $\text{H}_4\text{edtp}$ .** This ligand was prepared by a modification of the method given by Van Saun and Douglas.<sup>17</sup> From 142 g (1.3 mol) of 3-chloropropionic acid, 87 g (2.2 mol) of NaOH, and 14 cm<sup>3</sup> (0.23 mol) of ethylenediamine was obtained 12 g of a mixture that contained  $\text{H}_4\text{edtp}$ .

The pure  $\text{H}_4\text{edtp}$  was obtained by a gel filtration technique using G-10 Sephadex. The mixture (1.5 g) was passed through a column (40 cm ×

5 cm) with use of distilled water for elution. The eluate was monitored by pH (pH ~3-4 for pure  $\text{H}_4\text{edtp}$ ) or by testing for  $\text{Cl}^-$ . The eluate containing  $\text{H}_4\text{edtp}$  was evaporated to dryness; yield 0.7 g. Anal. Calcd for  $\text{H}_4\text{edtp}$ ,  $\text{C}_{14}\text{H}_{24}\text{O}_8\text{N}_2$  ( $M_r$  348.36): C, 48.27; H, 6.94; N, 8.04. Found: C, 48.11; H, 6.99; N, 7.80.

**Preparation of Sodium (Ethylenediaminetetrapropionato)rhodate(III) Dihydrate,  $\text{Na}[\text{Rh}(\text{edtp})]\cdot 2\text{H}_2\text{O}$ .** Rhodium trichloride trihydrate (1.32 g, 5 mmol) was dissolved in 3 cm<sup>3</sup> of water in a Pyrex tube. To this mixture was added a solution obtained by dissolving 1.74 g (5 mmol) of  $\text{H}_4\text{edtp}$  in 5 cm<sup>3</sup> of 4 M NaOH (20 mmol). The tube was sealed and the mixture heated at 145 °C in a oil bath for 7 h. After that the mixture was cooled to room temperature and the tube was chilled in ice and opened carefully. The yellow solution obtained was filtered off, and the filtrate was then introduced into a 55 cm × 4.5 cm column containing QAE A-25 Sephadex anion-exchange resin in the  $\text{Cl}^-$  form. NaCl solution (0.1 M) was used for elution (ca. 0.5 cm<sup>3</sup>/min). The eluate with -1 charge was obtained and evaporated under vacuum at 40 °C to a volume of 10 cm<sup>3</sup> and then cooled overnight in a refrigerator. The deposited NaCl was removed and the filtrate was desalted by passage through a G-10 Sephadex column, eluting with distilled water. Then the eluate was concentrated to a volume of 5 cm<sup>3</sup>. After the addition of 15 cm<sup>3</sup> of ethanol, the solution was left in a refrigerator for 4 days. The crystals were collected, washed with ethanol and then ether, and air-dried; yield 1.2 g (47%). Anal. Calcd for  $\text{Na}[\text{Rh}(\text{edtp})]\cdot 2\text{H}_2\text{O}$ ,  $\text{NaRhC}_{14}\text{H}_{24}\text{O}_{10}\text{N}_2$  ( $M_r$  506.25): C, 33.22; H, 4.77; N, 5.53. Found: C, 32.34; H, 5.04; N, 5.80.

### Resolution of Sodium (Ethylenediaminetetrapropionato)rhodate(III)

- (1) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549.
- (2) Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.
- (3) Dwyer, F. P.; Garvan, F. L. *J. Am. Chem. Soc.* **1960**, *82*, 4823.
- (4) Ogino, H.; Chung, J. J.; Tanaka, N. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 125.
- (5) Ezerskaya, N. A.; Filimonova, V. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1963**, *8*, 424.
- (6) Weyh, J. A.; Hamm, R. E. *Inorg. Chem.* **1968**, *7*, 2431.
- (7) Neal, J. A.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1226.
- (8) Majer, J.; Springer, V.; Kopecka, B. *Chem. Zvesti* **1966**, *20*, 414.
- (9) Neal, J. A.; Rose, N. J. *Inorg. Chem.* **1968**, *7*, 2405.
- (10) Neal, J. A. Ph.D. Dissertation, Washington State University, 1972.
- (11) Chaberek, S., Jr.; Martell, A. E. *J. Am. Chem. Soc.* **1952**, *74*, 6228.
- (12) Byers, W.; Douglas, B. E. *Inorg. Chem.* **1972**, *11*, 1470.
- (13) Gailey, K. D.; Radanović, D. J.; Djuran, M. I.; Douglas, B. E. *J. Coord. Chem.* **1978**, *8*, 161.
- (14) Radanović, D. J.; Gailey, K. D.; Djuran, M. I.; Douglas, B. E. *J. Coord. Chem.* **1980**, *10*, 115.
- (15) Radanović, D. J.; Gailey, K. D.; Djuran, M. I.; Douglas, B. E. *J. Coord. Chem.* **1982**, *11*, 247.
- (16) 1970 IUPAC Rules: *Pure Appl. Chem.* **1971**, *28*, 1. *Inorg. Chem.* **1970**, *9*, 1.
- (17) Van Saun, C. W.; Douglas, B. E. *Inorg. Chem.* **1969**, *8*, 1145 and references therein.

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**Table I.** Numerical Data of Absorption and Circular Dichroism (CD) Spectra<sup>a</sup>

complex ion	abs		CD			ref
	$\nu$ , $10^3$ $\text{cm}^{-1}$	$\epsilon$	$\nu$ , $10^3$ $\text{cm}^{-1}$	$\Delta\epsilon$		
$(-)_D$ - <i>trans</i> ( $O_5$ )-[Rh(edda)] <sup>-</sup>	~26.45 (sh)	405	29.41	-2.10	$^1E_g^a$	14
	29.85	745			$A_{2g}^a$	
	~33.89 (sh)	480	34.96	+0.36	$B_{2g}^a, E_g^b$	
$(-)_D$ -[Rh(1,3-pdta)] <sup>-</sup>	27.94 (sh)	284	25.51	-1.03	$E_g^a$	15
	29.58 (sh)	274	30.03	+2.05	$A_{2g}^a$	
	34.13	243	34.01	-0.65	$B_{2g}^a, E_g^b$	
			38.02	+0.09	$E_g^b$	
$(+)_D$ -[Rh(edtp)] <sup>-</sup>	~26.25 (sh)	240	25.19	-2.81	$E_g^a$	this work
	29.15	535	28.25	+5.77	$A_{2g}^a$	
	~33.20 (sh)	325	34.72	-1.06	$B_{2g}^a, E_g^b$	
			37.88	-0.56	$E_g^b$	

<sup>a</sup> Assignments are for  $D_{4h}$ .

**Dihydrate, Na[Rh(edtp)]·2H<sub>2</sub>O.** This complex (1.01 g, 2 mmol) was dissolved in 3 cm<sup>3</sup> of water and converted from the Na<sup>+</sup> to the H<sup>+</sup> form by passing the solution through a cation-exchange column. To the eluate was added an equivalent amount of strychnine (str; 0.67 g, 2 mmol), and the mixture was stirred with heating (50 °C) for 30 min. The solution obtained was filtered and evaporated to a volume of 5 cm<sup>3</sup>, and then to this solution was added 10 cm<sup>3</sup> of acetone and the solution was refrigerated for 3 days. The precipitated less soluble diastereoisomer  $(-)_D$ -*str*-(+)<sub>D</sub>-[Rh(edtp)]·6H<sub>2</sub>O, was removed, washed with acetone and then ether, and air-dried (0.5 g). It was crystallized from a 1:3 water-acetone mixture to a constant value of optical rotation. Aqueous solutions (0.1%) gave  $[\alpha]_D = +2^\circ$  or  $[\alpha]_{436} = -177^\circ$ . The more soluble diastereoisomer,  $(-)_D$ -*str*-( $-)_D$ -[Rh(edtp)]·xH<sub>2</sub>O, could not be isolated in pure form from the filtrate.

The enantiomer of the  $(+)_D$ -[Rh(edtp)]<sup>-</sup> was isolated in the form of its sodium salt by dissolving the diastereoisomer in water and passing the solution through a cation-exchange column in the Na<sup>+</sup> form. The eluate was evaporated under vacuum to a volume of 2 cm<sup>3</sup>, and the enantiomer was crystallized after adding 6 cm<sup>3</sup> of ethanol and cooling in the refrigerator for 3 days;  $[\alpha]_D = +30^\circ$  or  $[\alpha]_{436} = -250^\circ$  in 0.1% aqueous solution. Anal. Calcd for  $(-)_D$ -*str*-(+)<sub>D</sub>-[Rh(edtp)]·6H<sub>2</sub>O RhC<sub>35</sub>H<sub>55</sub>O<sub>16</sub>N<sub>4</sub> (*M*, 890.75): C, 47.20; H, 6.22; N, 6.29. Found: C, 47.35%; H, 6.00; N, 6.81. Anal. Calcd for  $(+)_D$ -Na[Rh(edtp)]·2H<sub>2</sub>O, NaRhC<sub>14</sub>H<sub>24</sub>O<sub>10</sub>H<sub>2</sub> (*M*, 506.25): C, 33.22; H, 4.77; N, 5.53. Found: C, 33.45; H, 4.94; N, 6.44.

**Physical Measurements.** The  $[\alpha]_\lambda$  values were measured in a 1-dm tube at 20 °C on a Perkin-Elmer SP polarimeter.

Infrared spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer using KBr disks.

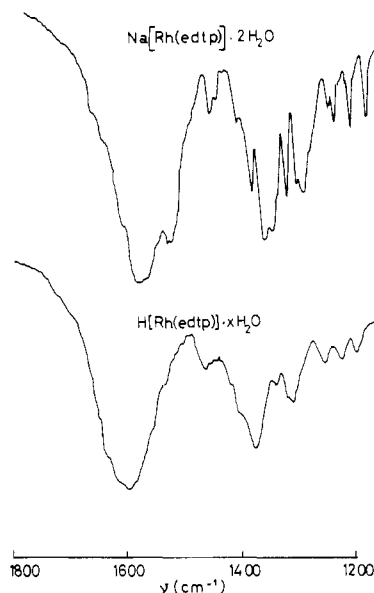
Electronic absorption spectra were recorded on a Varian SuperScan 3 recording spectrophotometer. For these measurements 10<sup>-3</sup> M aqueous solutions were used.

The circular dichroism curves were recorded at room temperature with a Jobin-Yvon Dichrographe III using a xenon arc source.

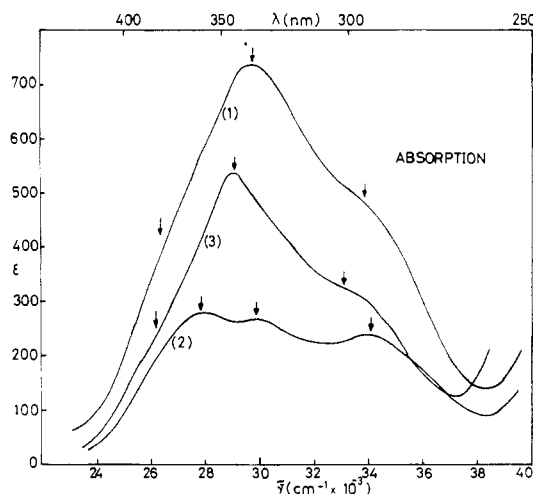
**Analysis.** Elemental microanalyses for carbon, hydrogen, and nitrogen were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade, Belgrade, Yugoslavia.

## Results and Discussion

**Infrared Spectra.** The asymmetric carboxylate stretching frequencies have been established as criteria for distinguishing between protonated carboxylate groups (1700–1750 cm<sup>-1</sup>) in metal aminopolycarboxylic acid complexes.<sup>18–20</sup> Also it has been demonstrated for tris(amino acidato)cobalt(III) complexes that the asymmetric stretching frequency of the carboxylate groups of the five-membered rings<sup>21</sup> lie at higher energy than the corresponding frequency of the six-membered chelate rings.<sup>22</sup> This was supported by Neal and Rose,<sup>7,9</sup> who found for *trans*( $O_5$ )-[M(SS-edds)]<sup>-</sup> complexes two very strong and well-separated bands in the asymmetric stretching carboxylate frequency region.



**Figure 1.** Portions of the infrared spectra of [Rh(edtp)]<sup>-</sup> complexes.



**Figure 2.** Electronic absorption spectra of (1) *trans*( $O_5$ )-[Rh(edda)]<sup>-</sup>, (2) [Rh(1,3-pdta)]<sup>-</sup>, and (3) [Rh(edtp)]<sup>-</sup>.

Later, similar results were obtained for [M(edda)]<sup>-</sup> complexes.<sup>23</sup>

The coordinated ethylenediaminetetrapropionate (edtp) ligand, in which four carboxylate groups are lengthened by one carbon atom each with respect to edta, forms four six-membered carboxylate rings. The Na[Rh(edtp)]·2H<sub>2</sub>O complex exhibits only one very strong band in the expected region (at ca. 1600 cm<sup>-1</sup>, see Figure 1), indicating that all carboxylate groups are coor-

(18) Busch, D. H.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4574; **1956**, *78*, 716.

(19) Morris, M. L.; Busch, D. J. *J. Am. Chem. Soc.* **1956**, *78*, 5178.

(20) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1963.

(21) Nakamoto, K.; Morimoto, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1961**, *83*, 4528.

(22) Celap, M. B.; Niketic, S. R.; Janjic, T. J.; Nikolic, V. N. *Inorg. Chem.* **1967**, *6*, 2063.

(23) Radanović, D. J.; Douglas, B. E. *J. Coord. Chem.* **1975**, *4*, 191.

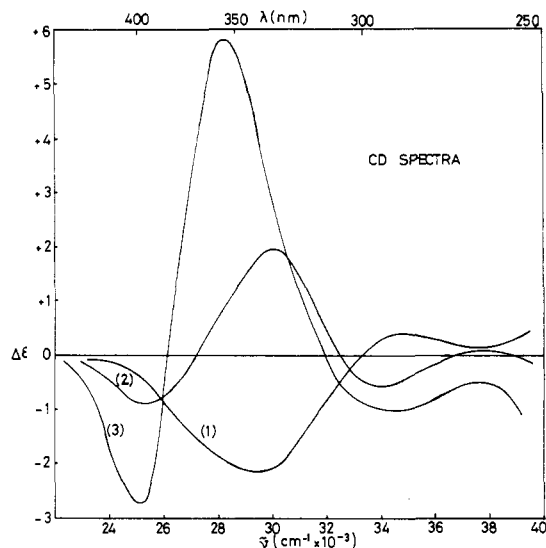


Figure 3. CD spectra of (1)  $(-)_D$ - $trans(O_5)$ -[Rh(eddda)]<sup>-</sup>, (2)  $(-)_D$ -[Rh(1,3-pdta)]<sup>-</sup>, and (3)  $(+)_D$ -[Rh(edtp)]<sup>-</sup>.

minated. Also the acid form of this complex, obtained by ion exchange, shows no evidence of protonated carboxylate groups in the expected (1700–1750  $cm^{-1}$ ) spectral region.

**Electronic Absorption and CD Spectra.** The electronic absorption and CD data for the [Rh(edtp)]<sup>-</sup> complex are shown in Table I and in Figures 2 and 3. For comparison, the corresponding values of  $trans(O_5)$ -[Rh(eddda)]<sup>-13,14</sup> and [Rh(1,3-pdta)]<sup>-13,15</sup> sexidentate complexes are given also.

The absorption spectrum of [Rh(edtp)]<sup>-</sup> (Figure 2, Table I) shows evidence of broadening and splitting in the lower energy spin-allowed region as was observed for other sexidentate Rh(III) edta-type complexes.<sup>14,15</sup> The electronic absorption bands of the edtp complex are so broad that both spin-allowed regions are included in the same band manifold. These factors, along with the fact that Rh(III) is larger than Co(III) and Cr(III), support the idea that the Rh(III) complexes are more distorted and are of lower effective symmetry than the other M(III) edta-type complexes.<sup>12,17,23-25</sup>

The [Rh(edtp)]<sup>-</sup> complex has  $C_2$  symmetry. However, its electronic absorption spectrum shows only two components in the region of the lower energy  $T_{1g}(O_h)$  transition. No splitting is apparent for the higher energy  $T_{2g}(O_h)$  absorption band. Complexes of the edta type that show only two components in the  $T_{1g}(O_h)$  region have been treated as having holohedrized  $D_{4h}$  symmetry. Because the equatorial donor atoms (2 N and 2 O) are higher in the spectrochemical series than the axial donors (2 O),

the peaks at lower and higher energy are assigned to the  $E_g^a$  and  $A_{2g}(D_{4h})$  components, respectively.

As was shown earlier,<sup>15</sup> both  $\epsilon$  and  $\Delta\epsilon$  intensities for the [Rh(1,3-pdta)]<sup>-</sup> complex are significantly lower than those for the other Rh(III) edta-type complexes,<sup>14</sup> as expected because of the less rigid 1,3-pdta framework. Also the intensities of the electronic absorption bands are lower for [Rh(edtp)]<sup>-</sup> (see Figure 2) with respect to those of  $trans(O_5)$ -[Rh(eddda)]<sup>-</sup> and other Rh(III) complexes,<sup>14</sup> as might be expected because of the decrease in chelate ring strain.<sup>17</sup>

The CD spectra of sexidentate edta-type M(III) complexes have been treated in terms of  $C_2$  symmetry.<sup>12,17,23-27</sup> Mason has shown<sup>28</sup> that the signs of the Cotton effects for complexes with  $C_2$  symmetry are related to the parent levels in complexes with  $D_3$  symmetry having the same configuration. It was thought that the lower energy CD peaks (A ( $C_2$ ) or E ( $D_{4h}$ )) for edta-type complexes of  $d^3$  and low-spin  $d^6$  metal ions are positive for the  $\Lambda(\Delta\Delta)$  configuration.<sup>12,17,23-27</sup> The CD sign patterns ( $-$ , $+$ ) for [Rh(edta-type)]<sup>-</sup> complexes<sup>14,15</sup> do not correspond to that predicted by empirical correlations with Co(III) complexes, and the assignments of the absolute configurations of these complexes were made on the basis of the stereospecificity of the  $S,S$ -edds ligand.

The  $\Lambda$  absolute configurations for the  $(-)_D$  isomers of [Rh(1,3-pdta)]<sup>-</sup> and  $trans(O_5)$ -[Rh(eddda)]<sup>-</sup> complexes have recently been confirmed by X-ray structure analysis.<sup>29,30</sup> These results confirm that the stereospecificity of  $SS$ -edds provides a reliable basis for assigning absolute configurations and that the analogous CD sign patterns of corresponding Co(III) complexes do not. The CD spectrum of the  $(+)_D$  isomer of [Rh(edtp)]<sup>-</sup> (Figure 3) exhibits the ( $-$ , $+$ ) CD pattern in the lowest energy spin-allowed region, so that enantiomer is assigned the  $\Lambda$  absolute configuration also. Since the sign of the dominant CD peak has been used for assigning absolute configurations, it should be noted that this approach fails for  $trans(O_5)$ -[Rh(eddda)]<sup>-</sup> (Figure 3).

CD components of the less strained [Rh(edtp)]<sup>-</sup> complex are much more intense than those of other edta-type Rh(III) complexes,<sup>14</sup> a result not expected from some theories of optical activity.<sup>31,32</sup> This indicates a great effect of adding two more six-membered rings to the eddda complex.

**Registry No.** Na[Rh(edtp)], 98875-98-0;  $(-)_D$ -str- $(+)_D$ -[Rh(edtp)], 99031-66-0;  $(+)_D$ -Na[Rh(edtp)], 98973-87-6; H[Rh(edtp)], 98875-99-1;  $H_4$ edtp, 13311-39-2; 3-chloropropionic acid, 107-94-8; ethylenediamine, 107-15-3.

(24) Randanović, D. J.; Douglas, B. E. *Inorg. Chem.* **1975**, *14*, 6.

(25) Douglas, B. E.; Haines, R. A.; Brushmiller, J. G. *Inorg. Chem.* **1963**, *2*, 1194.

(26) Gillard, R. D. *Spectrochim. Acta* **1964**, *20*, 1431.

(27) Hawkins, C. J.; Larsen, E. *Acta Chem. Scand.* **1965**, *19*, 185, 1969.

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

(29) Herak, R.; Srdanov, G.; Djuran, M. I.; Radanović, D. J.; Bruvo, M. *Inorg. Chem. Acta* **1984**, *83*, 55.

(30) Herak, R.; Manojlović-Muir, Lj.; Djuran, M. I.; Radanović, D. J. *J. Chem. Soc., Dalton Trans.* **1985**, 861.

(31) Liehr, A. D. *J. Phys. Chem.* **1964**, *68*, 655.

(32) Piper, T. S.; Karipides, A. G. *Mol. Phys.* **1962**, *5*, 475. Karipides, A. G.; Piper, T. S. *J. Chem. Phys.* **1964**, *40*, 674.