

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
DREXEL UNIVERSITY, PHILADELPHIA, PENNSYLVANIA 19104***p*-Dioxane, *p*-Thioxane, and 1,2-Dimethoxyethane Complexes with Transition Metal Perchlorates<sup>1</sup>**

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Synthetic and characterization studies of 3d metal perchlorate complexes with *p*-dioxane (DX), *p*-thioxane (TX), and 1,2-dimethoxyethane (DME) are reported.  $\text{CuL}_4(\text{ClO}_4)_2$  complexes with DX and TX exhibit subnormal magnetic moments and were assigned structures involving binuclear, monodentate ligand-bridged complex cations, *i.e.*,  $[(\text{DX})_2\text{Cu}(\text{DX})_2\text{Cu}(\text{DX})_2](\text{ClO}_4)_4$  and  $[(\text{TX})_2(\text{O}_3\text{ClO})\text{Cu}(\text{TX})_2\text{Cu}(\text{OClO}_3)(\text{TX})_2](\text{ClO}_4)_2$ . The latter complex contains S-bonded bridging and both S- and O-bonded terminal TX ligands.  $[\text{Cu}(\text{DME})_2](\text{ClO}_4)_2$  is monomeric, with chelating bidentate DME ligands and a planar  $\text{CuO}_4$  moiety in the complex cation. A red Zn(II) complex with TX was assigned a structure involving a polynuclear sulfur-bridged complex cation  $([\text{Zn}(\text{TX})_2(\text{OH}_2)_2]_n(\text{ClO}_4)_{2n})$ . TX acts exclusively as a sulfur ligand in this complex. A yellow isomer of this compound contains TX bonded through both O and S and is probably monomeric with chelating TX groups in the boat conformation  $(\text{Zn}(\text{TX})_2(\text{OH}_2)_2)^{2+}$ . The rest of the complex cations involve monodentate DX or TX and chelating bidentate DME ligands. TX coordinates through sulfur in these complexes. These compounds were formulated as follows:  $[\text{M}(\text{DX})_2(\text{OH}_2)_4](\text{ClO}_4)_2$  (M = Mn, Co, Ni, Zn);  $[\text{M}(\text{TX})_2(\text{OH}_2)_4](\text{ClO}_4)_2$  (M = Mn, Fe);  $[\text{M}(\text{DME})_2(\text{OH}_2)_2](\text{ClO}_4)_2$  (M = Mn, Co, Ni, Zn) (these complexes involve distorted octahedral complex cations; and  $[\text{Fe}(\text{DX})_4]_n(\text{ClO}_4)_{2n}$  and  $[\text{Fe}(\text{DME})_2]_n(\text{ClO}_4)_{2n}$ , containing either tetracoordinated, monomeric or pentacoordinated, binuclear complex cations. Finally, Co(II) and Ni(II) salts react with TX, and dark-colored solids containing decomposition products of this ligand are precipitated.

**Introduction**

Complexes of *p*-dioxane (DX), *p*-thioxane (TX),<sup>2-13</sup> and 1,2-dimethoxyethane (DME),<sup>2h,4,6,14,15</sup> mostly with metal halides, have been the subject of many synthetic and characterization studies. DX and TX may act either as monodentate or as bridging bidentate ligands.<sup>2-12</sup> A structure involving a chelated DX ligand, in the boat conformation, was proposed for the yellow modification of  $\text{ZnCl}_2 \cdot \text{DX}$ .<sup>13</sup> In all the other reported complexes of DX and TX, it was assumed or established that these ligands retain the more stable chair conformation.<sup>2-12</sup> Aside from  $\text{TiCl}_3 \cdot \text{TX}$ , which in-

volves coordination of TX either through oxygen or through both O and S (bridging ligand),<sup>4</sup> and  $\text{MX}_4 \cdot \text{TX}$  (M = Ti, Zr; X = Cl, Br), which contains bridging O- and S-bonded TX ligands,<sup>11</sup> the TX metal complexes reported thus far were characterized as monomeric and involving coordination of the ligand through sulfur regardless of whether the metal ion is soft or hard.<sup>2g,h,3,5,7-9,12</sup> DME in the gauche conformation acts usually as a bidentate chelating agent,<sup>2h,4,6,15</sup> but complexes involving monodentate DME ligands have been also reported.<sup>2h,4</sup>

We have recently reported the synthesis and characterization of cationic 3d metal complexes with tetrahydrofuran (THF).<sup>16</sup> No analogous general studies for the DX, TX, and DME ligands have appeared in the literature; in fact, the only reported metal perchlorate complexes of these ligands are  $\text{AgClO}_4 \cdot 3\text{DX}$ <sup>2b,c</sup> and  $\text{MClO}_4 \cdot 3\text{TX}$  (M = Cu, Ag).<sup>7</sup> Hence, it was felt that a study in this direction was in order. By utilizing triethylorthoformate, a dehydrating agent,<sup>17</sup> we have been able to prepare a number of DX, TX, and DME complexes with divalent 3d metal perchlorates. The present paper deals with the syntheses and characterization of these compounds.

**Experimental Section**

**Synthetic Procedure.**—The ligands (Aldrich products) were utilized as received. The hydrated metal perchlorate is dissolved in a 1:1 mixture of triethylorthoformate-ethanol and warmed at 50° for *ca.* 1 hr, under stirring. Then an excess of ligand (molar ratio of ligand to salt, *ca.* 6:1 for DX or TX and 3:1 for DME) is added to the salt solution. The Cu(II) and Zn(II) complexes of TX precipitate immediately. The DX and DME complexes and the Mn(II) and Fe(II) complexes of TX are obtained in crystalline form, by allowing the great bulk of the solvent to evaporate (50°), adding a few milliliters of ligand, and stirring the resulting mixture at room temperature until a crystalline product is obtained. The new complexes are filtered in the drybox (dry nitrogen atmosphere), washed with anhydrous

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TABLE I  
ANALYSES AND PROPERTIES OF METAL PERCHLORATE COMPLEXES WITH *p*-DIOXANE, *p*-THIOXANE, AND 1,2-DIMETHOXYETHANE

Complex	Color	$\mu_{\text{eff}}$ , BM (300°K)	$\Delta M$ , $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ (25°, $10^{-3} M$ solution in $\text{CH}_3\text{NO}_2$ )	% C		% H		% Metal		% S	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Mn(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Pale beige	6.18	187	19.14	18.41	4.82	4.53	10.94	11.42		
Fe(DX) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Cream white	5.32	184	31.65	31.07	5.31	5.12	9.20	9.53		
Co(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Pink	5.17	180	18.99	18.60	4.78	4.46	11.65	11.97		
Ni(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Light green	3.84	185	18.99	19.17	4.78	4.47	11.60	11.25		
Cu(DX) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Aqua	1.20	181	31.25	30.73	5.24	5.19	10.33	10.59		
Zn(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	White	Diamagnetic	177	18.75	18.20	4.72	4.52	12.75	13.31		
Mn(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Off-white	6.13	154	17.99	17.50	4.53	4.54	10.28	10.62	12.00	11.34
Fe(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Light brown	5.37	191	17.96	18.16	4.52	4.87	10.44	10.82	11.98	12.40
Cu(TX) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Pale green	Slightly paramagnetic (10 <sup>6</sup> χ <sub>g</sub> = +0.07 cgsu)	128 <sup>a,b</sup>	28.30	28.81	4.75	4.76	9.36	10.05	18.89	19.60
Zn(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Yellow <sup>c</sup>	Diamagnetic	170	18.89	18.21	3.93	4.40	12.85	13.53	12.60	11.81
	Red <sup>c</sup>		161 <sup>b</sup>		18.34		4.22		13.21		12.00
Mn(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Light tan	6.13	167	20.44	19.83	5.14	4.88	11.68	11.75		
Fe(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Tan	5.21	175	22.09	21.49	4.63	4.75	12.86	13.08		
Co(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Pink	4.80	178	20.27	19.76	5.10	5.01	12.43	12.34		
Ni(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Turquoise	3.26	181	20.28	20.62	5.10	4.68	12.38	11.93		
Cu(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Green	1.98	184	21.68	21.40	4.55	4.71	14.35	14.12		
Zn(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Off-white	Diamagnetic	174	19.99	19.57	5.03	5.43	13.60	13.63		

<sup>a</sup>  $\Delta M$  for Cu(TX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> at various concentrations:  $10^{-3} M$ , 128;  $5 \times 10^{-4} M$ , 134;  $10^{-4} M$ , 144;  $5 \times 10^{-5} M$ , 162. <sup>b</sup>  $10^{-3} M$  solutions in nitromethane-acetone (these complexes are not completely soluble in nitromethane). <sup>c</sup> See Experimental Section.

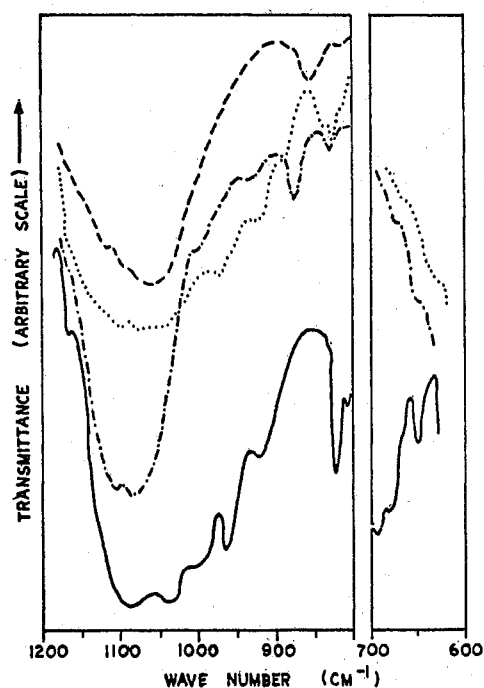


Figure 1.—Infrared spectra (1200–800 and 700–600  $\text{cm}^{-1}$ ): —, Cu(TX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>; - - - -, Zn(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (red complex); ····, Zn(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (yellow complex); - - - -, Fe(DX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>.

ether (DX, TX) or benzene and ligand (DME), and dried in an evacuated desiccator over P<sub>2</sub>O<sub>5</sub> or CaCl<sub>2</sub>.

The DX complexes with Fe(II) and Cu(II) are of the type M(DX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and stable in the atmosphere. The Mn(II), Co(II), Ni(II), and Zn(II) complexes with this ligand, initially obtained, are most probably of the type M(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>. These compounds are extremely moisture sensitive, as is also the case with DX or THF complexes of the halides of these metal ions.<sup>8,10,13,15</sup> In addition, during their storage in the evacuated desiccator they lose two ligand molecules and are converted to the stable M(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> complexes upon exposure to the atmosphere. Characterization studies were performed on the latter products. No attempts at the characterization of the unstable M(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> complexes

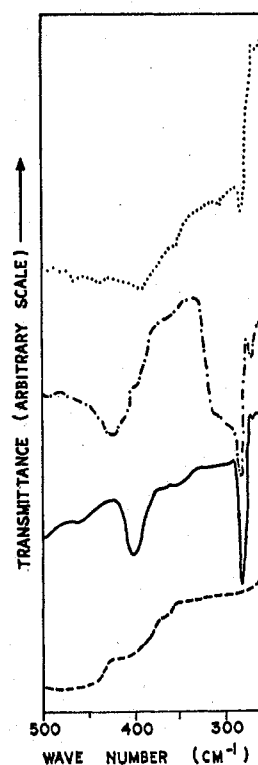


Figure 2.—Infrared spectra (500–250  $\text{cm}^{-1}$ ): —, Cu(TX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>; - - - -, Cu(DX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>; - - - -, Zn(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (red complex); ····, Zn(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>.

were made, because, despite our precautions, these compounds could not be obtained in a sufficiently pure state. *Anal.* Calcd for Co(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>: C, 29.75; H, 5.62; Co, 9.12. Found: C, 26.88; H, 6.42; Co, 7.67. Calcd for Ni(DX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>: C, 29.77; H, 5.62; Ni, 9.09. Found: C, 25.91; H, 5.78; Ni, 8.64.

The TX complexes precipitated are of the types Cu(TX)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and M(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>n</sub>(ClO<sub>4</sub>)<sub>2</sub> (M = Mn, Fe, Zn; n = 2, 4) and stable in the atmosphere. Co(II) and Ni(II) perchlorates apparently react with this ligand, yielding dark (almost black) colored precipitates of uncertain nature (analyses: Co(II)

TABLE II  
PERTINENT INFRARED DATA FOR METAL PERCHLORATE COMPLEXES WITH *p*-DIOXANE,  
*p*-THIOXANE, AND 1,2-DIMETHOXYETHANE (CM<sup>-1</sup>)<sup>a</sup>

Compound	700-600 cm <sup>-1</sup> region			T <sub>d</sub> ClO <sub>4</sub> <sup>-</sup> bands
	1200-800 cm <sup>-1</sup> region	(for TX complexes)	500-250 cm <sup>-1</sup> region <sup>d</sup>	
DX	1120 s*, 1110 w, 1081 s, 1046 m, 887 s, 874 s <sup>+</sup>		283 m, 273 m	
Mn(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	1112 s, sh*, 1040 sh, 850 m, vb <sup>+</sup>		390 w, 370 w, 342 w, 289 w, 279 s, 273 sh	1070 s, b, 620 s
Fe(DX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1118 s, sh*, 1099 s, sh*, 878 m, sh <sup>+</sup> , 859 m <sup>+</sup> , 829 sh <sup>+</sup>		400 m, b, 372 m, 346 sh, 279 s, 255 w, b	1060 s, 616 s
Co(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1105 s*, 1042 sh, 899 m, 870 s <sup>+</sup> , 823 m <sup>+</sup>		410 w, 380 m, b, 345 m, b, 278 m-s, 260 m, 251 w	1071 s, 915 sh, 617 s
Ni(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1115 s, vb*, 894 ms, 860 s <sup>+</sup> , 827 ms <sup>+</sup>		408 w, 389 m, 370 sh, 343 sh, 276 s, 261 w	1065 s, vb, 914 sh, 620 s
Cu(DX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1102 s, sh*, 1030 m, sh, 885 s, sh, 858 s <sup>+</sup> , 832 sh <sup>+</sup>		420 s, 395 sh, 350 sh, 279 s, 268 m, 252 w	1060 s, 910 sh, 610 s
Zn(DX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1105 s, b*, 902 s, 871 s <sup>+</sup> , 827 <sup>+</sup>		453 w, 430 w, 385 m, 350 sh, 279 s, 265 w, 252 w	1065 s, b, 920 sh, 612 s
TX	1172 s, 1105 vs*, 1050 m, 1006 vs, 993 sh, 969 vs, 956 sh, 865 m, 834 vs <sup>+</sup> , 809 s	693 m*, 664 s <sup>+</sup>	389 s, 340 w	
Mn(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	1172 sh, 1110-1080 s, vb*, 940 m, 830 w <sup>+</sup>	675 m, vb* <sup>+</sup>	480 w, b, 430 m, 390 w, 340 w, 270 m, 259 m	1110-1080 s, vb, 620 s
Fe(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1169 sh, 1101 sh*, 1004 sh, 955 sh, 872 m, 838 w <sup>+</sup>	665 sh*, 646 sh <sup>+</sup>	470 m, b, 415 sh, 389 sh, 370 sh, 271 m-s, 260 m	1080 s, b, 930 w, 615 s
Cu(TX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1168 m, 1040 s, <sup>b</sup> 1003 sh, 990 sh, 964 s, 832 sh <sup>+</sup> , 820 s <sup>+</sup> , 808 s	694 m*, 685 sh*, 649 m <sup>+</sup>	455 m, b, 399 s, 350 sh, 280 s, 270 w, 250 m, b	1090 s, 920 m, 620 s
Zn(TX) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> Yellow complex	1170 sh, 1098 s*, 1050 sh, 1000 sh, 976 m, 960 sh, 928 m, 902 sh, 840 m <sup>+</sup> , 829 s <sup>+</sup> , 819 sh <sup>+</sup>	670 sh*, 650 sh <sup>+</sup>	430, 390 sh, 325 sh, 275 m, b	1080 s, b, 928 m, 620 s
Red complex	1170 sh, 1105 s*, 1004 sh, 960 sh, 873 s, 828 m <sup>+</sup>	670 sh*, 640 sh <sup>+</sup>	475 m, b, 420 sh, 350 sh, 268 sh	1080 s, b, 928 m, 620 s
DME	1192 s, 1120 vvs <sup>+</sup> , 1030 s, 986 m, 940 m, 858 s <sup>+</sup>			
Mn(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1190 m, 1170 m, 1142 m-s, 970 m, b, 890 m, sh, 870 m, sh <sup>+</sup> , 831 w, sh <sup>+</sup>			1078 vs, 622 vs
Fe(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1169 m, 1146 m, 1050 sh, 1000 w, 980 m-s, b, 890 m-s, 840 w <sup>+</sup> , sh			1074 vs, 627 vs
Co(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1200 m, 1162 m, sh, 1150 m-s, 990 s, sh, 895 m, 848 m <sup>+</sup>			1085 vs, b, 624 vs
Ni(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1160 m, 1135 sh, 1014 m, 965 m, 890 m, 870 m <sup>+</sup> , 837 m <sup>+</sup> , 800 sh			1080 vs, b, 626 vs
Cu(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1190 sh, 1162 sh, 970 m, 930 w, 880 w <sup>+</sup> , 810 m <sup>+</sup>			1080 vs, 620 vs
Zn(DME) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	1190 sh, 1140 s, b, 1019 sh, 970 m, 887 m, 828 m <sup>+</sup>			1076 vs, 618 vs

<sup>a</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. The symbols \* and + denote bands associated with  $\nu_{C-Y-C}$  asymmetric and symmetric, respectively (Y = O or S);  $\nu_{C-O-C}(\text{asym})$  is masked by the intense  $\nu_3(\text{ClO}_4)$  band in the DME complexes (see text); the bands at 1160-1135 cm<sup>-1</sup> in these complexes may be due to a splitting of  $\nu_{C-O-C}(\text{asym})$ <sup>18</sup> ( $\nu_{C-O-C}(\text{sym})$  is also probably split in certain cases). <sup>b</sup> This band is due to a splitting of the  $\nu_3(\text{ClO}_4)$  mode. <sup>c</sup> No satisfactory resolution could be obtained for the spectra of the Mn(II) complexes with DX and TX. <sup>d</sup> The low-frequency ir spectra of the DME complexes show extremely poor resolution.

product: Co, 14.87; C, 5.36; H, 3.73; S, 4.51. Ni(II) product: Ni, 15.60; C, 3.03; H, 3.47; S, 3.10). Dark colored solids were also obtained during reaction of TX with Co(II) and Ni(II) acetates, nitrates, and halides, under the experimental conditions of this work. Interesting color changes are observed during storage of the Zn(II)-TX complex in the desiccator (under vacuum). This compound is initially obtained as a white precipitate, which is presumably a higher hydrate (*i.e.*, Zn(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>); when dried over P<sub>2</sub>O<sub>5</sub> it is converted to a bright red solid; however, when CaCl<sub>2</sub> is the drying agent, it yields a yellow solid. Analyses of both these products are consistent with the formula Zn(TX)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (*cf.* Table I). These colored Zn(II) complexes yield colorless solutions in organic solvents (acetone, nitromethane, etc.).

The DME complexes are also initially obtained as hydrates. The Fe(II) and Cu(II) compounds lose water in the desiccator yielding anhydrous products of the type M(DME)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>. The Fe(II) complex is only slightly hygroscopic while the Cu(II) compound is extremely moisture sensitive. The Mn(II), Co(II), Ni(II), and Zn(II) complexes M(DME)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> retain coordinated water, even after prolonged storage in the desiccator.

The new DME complexes are generally insoluble in the parent ether, but dissolve in many organic solvents (*e.g.*, nitromethane, acetone). The DX and TX complexes are, in most cases, soluble in the parent ethers and organic solvents. Analyses (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.) and some properties of the complexes under study are given in Table I.

**Spectral, Magnetic, and Conductance Measurements.**—Infrared spectra (Nujol mulls; Table II, Figures 1, 2), electronic spectra (Table III, Figure 3), and magnetic and conductance (Table I) measurements were obtained by methods previously described.<sup>18</sup> Attempts to grind the new complexes, in order to obtain X-ray powder diffraction patterns, were unsuccessful; these compounds collapse to viscous liquids during grinding in the drybox (N<sub>2</sub> atmosphere).

## Discussion

### Infrared and Conductance Data.—The ir spectra of

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TABLE III  
ELECTRONIC SPECTRA OF *p*-DIOXANE, *p*-THIOXANE, AND  
1,2-DIMETHOXYETHANE METAL COMPLEXES

Complex	Medium	$\lambda$ , nm ( $\epsilon$ max)
Fe(DX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	209 vs, 389 sh, 902 s, sh, 1200 b, sh, 938 (5)
Co(DX) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	208 vs, 238 vs, 461 s, sh, 496 s, 538 s, sh, 1180 w, vb, 492 sh (243), <sup>a</sup> 1237 (4.2)
Ni(DX) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	216 vs, 240 vs, 263 vs, 371 s, 660 m, 765 sh, 1150 w, vb, <380, 630 (4.5), 726 sh, 1200 b (1.7)
Cu(DX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	223 vs, sh, 258 vs, 683 m, b, 940 m, sh, 592 (29)
Fe(TX) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	220 vs, 275 vs, 400 s, sh, 700- 1500 m, vb (maxima at 780 and 1425), 1036 (17), 1301 (11)
Cu(TX) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol, 10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub> and acetone	209 vs, 254 vs, 423 s, sh, 460 s, 652 m, b, 935 m, 601 (43)
Zn(TX) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>		
Yellow complex <sup>b</sup>	Nujol	209 vs, 275 vs, 338 sh
Red complex <sup>b</sup>	Nujol	209 vs, 275 vs, sh, 425 s, 552 s
Mn(DME) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol	<300 vs
Fe(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol	<300 vs, 904 m, b, 1200 m, sh
Co(DME) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol	465 s, sh, 502 s, 548 s, sh, 1270 m, b
Ni(DME) <sub>2</sub> (OH) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol	392 s, 710 s, b, 1100 m, b
Cu(DME) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Nujol	799 vs

<sup>a</sup> This band occurs as a shoulder of an intense charge-transfer absorption. <sup>b</sup> Both Zn(II)-*p*-thioxane complexes produce colorless solutions in various organic solvents (e.g., nitromethane, acetone, etc.).

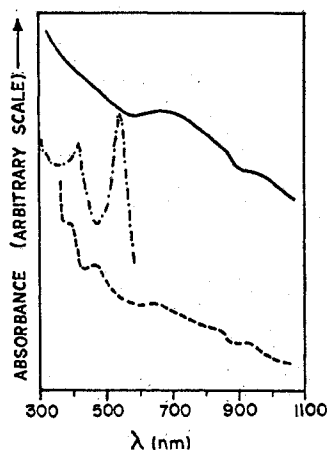


Figure 3.—Solid-state visible spectra: —, Cu(DX)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>; ---, Cu(TX)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>; - · - · -, Zn(TX)<sub>2</sub>(OH)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (red complex).

the ligands under study and their metal complexes have been extensively studied.<sup>2-11,13-15,19</sup> In the cases of DX and DME, complex formation results in negative shifts and/or splittings of the bands associated with  $\nu_{C-O-C}$  ( $\nu_{C-O-C}$  asymmetric and symmetric, respectively: DX 1120, 874 cm<sup>-1</sup>,<sup>8</sup> DME 1120, 858 cm<sup>-1</sup> 6). When these ligands are coordinated through both their etheric oxygens (bridging DX and chelating DME groups), the  $\nu_{C-O-C}$  bands of the free ligands disappear.<sup>2d,h,4,6,8</sup> Free TX exhibits the following absorptions in the  $\nu_{C-O-C}$  and  $\nu_{C-S-C}$  regions: 1200-800 cm<sup>-1</sup>: 1172 s, 1105 vs ( $\nu_{C-O-C}$ , asym), 1050 m, 1006 vs, 993 sh, 969 vs, 956 sh, 865 w, 834 vs ( $\nu_{C-O-C}$ , sym),

809 s; 700-650 cm<sup>-1</sup>: 693 m, 664 s ( $\nu_{C-S-C}$  bands).<sup>7,19</sup> Oxygen-bonded TX metal complexes exhibit negative shifts and splittings of the  $\nu_{C-O-C}$  modes.<sup>4</sup> In sulfur-bonded complexes of TX the  $\nu_{C-S-C}$  bands suffer a lowering in frequency and decrease in intensity.<sup>7,9</sup>

Cu(TX)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> exhibits ir bands attributable to the presence of both ionic and coordinated perchlorate.<sup>20</sup> Thus the  $\nu_3$ (ClO<sub>4</sub>) mode is clearly split, while  $\nu_1$  is ir active; splittings of  $\nu_4$  cannot be detected, owing to the presence of  $\nu_{C-S-C}$  absorptions in the 650-600 cm<sup>-1</sup> region (Table II, Figure 1). The presence of coordinated perchlorate in this complex is also supported by the fact that it shows a behavior intermediate between 1:1 and 2:1 electrolytes in nitromethane (Table I). The rest of the new complexes behave as 2:1 electrolytes in nitromethane and do not exhibit any  $\nu_3$ (ClO<sub>4</sub>) splittings; in certain of these complexes (Table I)  $\nu_1$  is weakly ir active. The complexes involving coordinated aquo ligands (Table I) exhibit the characteristic  $\nu_{OH}$  and  $\delta_{H-O-H}$  bands at 3500-3400 and 1640-1620 cm<sup>-1</sup><sup>21</sup> and, as was the case with THF analogs,<sup>16</sup> absorptions attributable to the rocking (750-640 cm<sup>-1</sup>) and wagging (560-530 cm<sup>-1</sup>) modes of coordinated water.<sup>22</sup> The  $\nu_{C-Y-C}$  (Y = O or S) bands of the free ligands show the following changes in the new complexes (Table II, Figure 1). In the case of DX complexes, split  $\nu_{C-O-C}$  (asymmetric and symmetric) bands are observed; the higher energy  $\nu_{C-O-C}$  bands occur at frequencies quite close to those of the corresponding absorptions in free DX while the lower energy ones exhibit large negative shifts. This evidence suggests that the new DX complexes involve, at least partially, monodentate DX ligands coordinating through one of the etheric oxygens.<sup>7,9</sup> The spectra of the DME complexes exhibit great similarities to those reported for metal halide complexes with this ligand.<sup>15</sup> Bands attributable to uncoordinated O sites (i.e., at ca. 1120 and 858 cm<sup>-1</sup>)<sup>2d,h,4,6,8,15</sup> are not observed;  $\nu_{C-O-C}$  (asym) is, presumably, masked by the intense  $\nu_3$ (ClO<sub>4</sub>) absorption, while  $\nu_{C-O-C}$ (sym) shows the characteristic splittings observed in the spectra of DME metal chelates.<sup>15</sup> It is, thus, reasonable to conclude that in the new complexes DME, in the gauche conformation, acts as a bidentate chelating agent.<sup>15</sup> TX clearly acts as a monodentate S ligand in the Mn(II), Fe(II), and the red Zn(II) complexes; in fact, the  $\nu_{C-O-C}$  bands of this ligand remain practically unchanged in the above complexes, whereas the  $\nu_{C-S-C}$  bands show negative frequency shifts.<sup>7</sup> The yellow Zn(ClO<sub>4</sub>)<sub>2</sub>-TX complex exhibits ir spectra characterized by splittings of the  $\nu_{C-O-C}$ (sym) mode and negative  $\nu_{C-S-C}$  frequency shifts. In this compound TX acts apparently as a bidentate ligand coordinating through both O and S. Finally in the spectra of Cu(TX)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, the positions of the split  $\nu_{C-O-C}$ (sym) and  $\nu_{C-S-C}$  absorptions are indicative of the presence of mixed O and S coordination sites as well as uncoordinated O and S sites. An analogous case is that of [Pd(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (DMSO = dimethyl sulfoxide), in which two ligands coordinate through oxygen and the other two through sulfur.<sup>23</sup> TX apparently behaves in a similar way in the Cu(II) complex. With the exception of the Cu(II)

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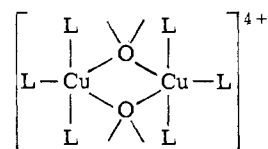
(23) B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, **8**, 971 (1969).

complexes with DX and TX, the new complexes could not produce satisfactory Nujol mulls, and their low-frequency ir spectra were of very poor quality (Figure 2); no band assignments are attempted in these cases.  $\nu_{\text{Cu-O}}(\text{DX or TX})$  is tentatively assigned to the bands at 420 (DX complex) and 399 (TX complex)  $\text{cm}^{-1}$ ; the bands at 350 and 280  $\text{cm}^{-1}$  in the spectrum of  $\text{Cu}(\text{TX})_4(\text{ClO}_4)_2$  are probably due to  $\nu_{\text{Cu-O}}$  (perchlorate)<sup>24,25</sup> and  $\nu_{\text{Cu-S}}$ , respectively.

**Electronic Spectra and Magnetic Moments. Formulation of the Complexes.**—The electronic spectra of the Co(II) and Ni(II) complexes with DX and DME are characteristic of hexacoordinated compounds of these metal ions (Table III). The splittings observed in the (d-d) bands of the Co(II) complexes are suggestive of an effective symmetry lower than  $O_h$ .<sup>26</sup> The spectrum of  $\text{Fe}(\text{TX})_2(\text{OH}_2)_4(\text{ClO}_4)_2$  is also indicative of a distorted octahedral configuration; this is suggested by the splittings of the (d-d) band.<sup>27</sup> The magnetic moments of the hexacoordinated complexes are generally either within the "octahedral" region for these metal ions or slightly higher<sup>28</sup> ( $\text{Ni}(\text{DX})_2(\text{OH}_2)_4(\text{ClO}_4)_2$  has a  $\mu_{\text{eff}}$  of 3.34 BM). The above data, in combination with the ir and conductance evidence, lead to the following formulations for the hexacoordinated complexes:  $[\text{M}(\text{DX})_2(\text{OH}_2)_4](\text{ClO}_4)_2$  ( $\text{M} = \text{Mn, Co, Ni, Zn}$ ),  $[\text{M}(\text{DME})_2(\text{OH}_2)_2](\text{ClO}_4)_2$  ( $\text{M} = \text{Mn, Co, Ni, Zn}$ ), and  $[\text{M}(\text{TX})_2(\text{OH}_2)_4](\text{ClO}_4)_2$  ( $\text{M} = \text{Mn, Fe}$ ). The fact that the  $\nu_1$  mode of ionic  $\text{ClO}_4^-$  is weakly ir active in certain of these complexes (*vide supra*) is apparently due to local site symmetry lowering of the perchlorate ion in the crystal lattice<sup>24,25</sup> rather than the presence of weakly coordinated perchlorate ligands. The complex cations are probably distorted octahedral. DX and TX act as monodentate ligands in these complexes, the latter coordinating through its sulfur atom. DME acts as a bidentate chelating agent. It is noteworthy that 1,2-dimethylthioethane (DMTE) reportedly forms a tris-chelate complex of the type  $[\text{Ni}(\text{DMTE})_3](\text{ClO}_4)_2$ .<sup>29</sup> In the case of DME, formation of tris chleates with the above metal ions is presumably impeded by the competition between ligand and aquo groups in the first coordination sphere of the metal ion. Mixed-ligand (*i.e.*, ether-aquo) complexes of the same metal perchlorates were also obtained during their interaction with THF.<sup>16</sup> Ethers generally give rise to weaker ligand fields than aquo groups, and competition between these two types of ligands for the metal ion should be expected.<sup>4,30</sup> The aquo groups in the hydrated DX, TX, and DME complexes apparently form strong covalent bonds with the metal ion, as indicated by the fact that they cannot be removed by prolonged desiccation over a number of effective drying agents ( $\text{P}_2\text{O}_5$ ,  $\text{Mg}(\text{ClO}_4)_2$ , or  $\text{CaCl}_2$ ).

The new Cu(II) complexes are anhydrous; Cu-

$(\text{DME})_2(\text{ClO}_4)_2$  is magnetically normal and exhibits a sharp and strong (d-d) band at 799 nm. This compound most probably involves a cationic bis-chelate complex cation, with a planar  $\text{CuO}_4$  moiety<sup>16,31</sup> ( $[\text{Cu}(\text{DME})_2](\text{ClO}_4)_2$ ). The arrangement of the DME ligands in space probably introduces lower symmetry components into the ligand field,<sup>26</sup> so that the effective symmetry of the complex cation becomes lower than  $D_{4h}$ . In contrast the  $\text{CuL}_4(\text{ClO}_4)_2$  ( $\text{L} = \text{DX, TX}$ ) complexes are magnetically subnormal (Table I), and their electronic spectra are characterized by splittings of the (d-d) band (Table III, Figure 3). The magnetic properties of these complexes may be attributed to binuclear, ligand-bridged structures.<sup>32</sup> Subnormal magnetic moments in binuclear Cu(II) complexes of this type arise from spin-spin interactions through a superexchange mechanism, operating *via* the bridging ligand atoms.<sup>32</sup> On the other hand, splittings of the (d-d) band in Cu(II) complexes have been reported for penta-<sup>33</sup> and tetragonally distorted hexacoordinated compounds.<sup>26,27</sup> The overall evidence is favoring a structure involving a binuclear, pentacoordinated, DX-bridged complex cation of the type



for  $\text{Cu}(\text{DX})_4(\text{ClO}_4)_2$ , which is, therefore, formulated as  $[(\text{DX})_3\text{Cu}(\text{DX})_2\text{Cu}(\text{DX})_3](\text{ClO}_4)_4$ . An essentially similar structure is rather improbable for the TX analog; in fact, the magnetic moments of the two complexes are quite different (the DX complex shows a  $\mu_{\text{eff}}$  of 1.20 BM, while the TX complex is only slightly paramagnetic); in addition  $\text{Cu}(\text{TX})_4(\text{ClO}_4)_2$  involves coordination of one perchlorato ligand (*vide supra*). A binuclear, TX-bridged structure involving coordination of the bridging monodentate TX ligands through sulfur would lead to an enhancement of the exchange coupling through the bridge, in comparison to that occurring in systems containing  $\text{CuO}_2\text{Cu}$  bridges.<sup>34</sup> Thus, a formulation of the type  $[(\text{TX})_3(\text{O}_3\text{ClO})\text{Cu}(\text{TX})_2\text{Cu}(\text{OClO}_3)(\text{TX}_3)](\text{ClO}_4)_2$ , involving a hexacoordinated complex cation containing monodentate, S-bonded, bridging TX ligands and monodentate, terminal perchlorato and TX ligands, appears to be the most compatible with the spectral, magnetic, and conductance evidence; one or more of the terminal TX ligands are O bonded (*vide supra*). The anhydrous Fe(II) complexes  $(\text{Fe}(\text{DX})_4(\text{ClO}_4)_2)$  and  $(\text{Fe}(\text{DME})_2(\text{ClO}_4)_2)$  exhibit electronic spectra which may be attributed to either a low-symmetry (*e.g.*,  $D_{2d}$ ) tetraordinated configuration involving monomeric complex cations<sup>18,35</sup> or a pentacoordinated binuclear ligand-bridged structure.<sup>33</sup> They are, thus, formulated as  $[\text{Fe}(\text{DX})_4]_n(\text{ClO}_4)_{2n}$  and  $[\text{Fe}(\text{DME})_2]_n(\text{ClO}_4)_{2n}$  ( $n = 1$  or  $2$ ).

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(32) W. H. Watson, *Inorg. Chem.*, **8**, 1879 (1969); M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964), and references therein.

(33) M. Ciampolini, *Struct. Bonding (Berlin)*, **6**, 52 (1969), and references therein.

(34) We wish to thank one referee for drawing our attention to this point.

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Finally, the two colored Zn(II)-TX complexes have, undoubtedly, unusual structures. The yellow Zn(II) complex involves bidentate TX ligands (*vide supra*) and may be either polynuclear with bridging TX groups in the chair conformation or monomeric with chelating TX ligands in the boat conformation; distinction between the chair and boat conformation of TX is rather unlikely because of their low basic symmetry ( $C_2$ ).<sup>7</sup> It is, however, noteworthy that in the only yellow Zn(II) complex with DX the ligand is in the boat conformation.<sup>13</sup> A white polymeric analog of this compound, involving bridging DX groups has also been reported.<sup>2a,3</sup> It is, thus, possible that the yellow Zn(II) complex involves a monomeric complex cation involving two chelating TX groups in the boat conformation and two aquo groups and coordination number six for the Zn(II) ion. In the rest of the TX and in the DX complexes reported, the ligands apparently retain the more stable chair conformation. The formation of an intensely red colored complex of Zn(II) with a colorless ligand<sup>36</sup> was quite unexpected. The limited solubility of this complex in

(36) J. Barrett and M. J. Hitch, *Spectrochim. Acta, Part A*, **25**, 407 (1969).

nitromethane may be indicative of a polymeric structure. In addition, the fact that the red compound forms colorless solutions in organic solvents demonstrated that the structure responsible for the red color is stable only in the solid state. An analogous case reported in the literature is the red polymeric complex of Sn(IV), formed during reduction of benzene-1,2-disulfonyl chloride with tin and hydrochloric acid.<sup>37</sup> In fact, this polynuclear compound, which involves bridging S ligands, exhibits a visible spectrum similar to that of the red Zn(II) complex (Table III, Figure 3) and forms colorless solutions in the organic solvents in which it is soluble.<sup>37</sup> Further, monomeric Sn(IV) complexes with analogous sulfur ligands are colorless.<sup>37</sup> The assignment of a bi- or polynuclear structure involving both terminal and bridging monodentate TX groups acting exclusively as S ligands (*vide supra*) to the red Zn(II) complex is justified from the above discussion. The yellow Zn(II) compound is, therefore, formulated as  $[Zn(TX)_2(OH_2)_2](ClO_4)_2$  and the red complex as  $[Zn(TX)_2(OH_2)_2]_n(ClO_4)_{2n}$  ( $n = 2$  or higher).

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## Modes of Intramolecular Rearrangement in Octahedral Complexes

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The types or modes of rearrangement of an octahedral complex are examined in detail. The behavior of tris-chelate complexes under each of these modes is considered and recent nmr experiments on  $M(AB)_3$  complexes are interpreted in terms of split modes. It is pointed out that the experiments cannot distinguish between a mode of rearrangement which involves racemization and one which does not.

### 1. Introduction

Intramolecular rearrangements in octahedral complexes have been of interest since the time of Werner<sup>1</sup> and recent experiments,<sup>2-12</sup> mainly using nmr, have prompted the analysis of some of the possible mechanisms involved.<sup>1c,13-15</sup> There has, however, been no

general description in the literature of *all* the theoretically possible rearrangements<sup>16</sup> so that no unambiguous analysis of the experiments could be carried out.

The present article is concerned with an enumeration of all the physically distinguishable intramolecular rearrangements of an arbitrary octahedral complex in which the nature of the individual ligands is assumed to be of secondary importance. The argument follows precisely the argument given previously<sup>17</sup> for trigonal-bipyramidal molecules and is based on the description of intramolecular rearrangements of molecules with skeletons possessing any symmetry whatsoever in terms of sets of like processes or "modes of rearrangement." A mode of rearrangement refers to a class of stereoisomerizations in which the relative orientation of a certain subset of all the ligands changes. Thus each mode of rearrangement can be defined as a class of rearrangements in which  $x$  ligands retain their rela-

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- (16) After this article was completed, we received from Professor M. Gielen a copy of his study which gives such an analysis although it does not discuss any of the experimental results. This analysis has not been referred to in any of the aforementioned experimental analyses. We are grateful to Professor Gielen for his kindness in calling this to our attention and also for having sent a preprint of his review article scheduled to appear in "Graph Theory," A. Balaban, Ed., Academic Press, New York, N. Y., 1972. [M. Gielen and N. Vanlanten, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970).]
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