valence pairs and in view of the naiveté of the model itself. Nevertheless, the observed nonequivalence between the lone pair and bonding pairs is not in the direction predicted by Gillespie's rules,[2] since the lone pair of xenon occupies a much smaller portion of the valence shell than do the bonding pairs to fluorines. It is possible that a model in which the effective value of n depends upon molecular environment could extend the utility of the present model. We must conclude, however, that the points-on-a-sphere model has at best a limited utility for geometries with more than six ligands.

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Coordination Compounds of 2,5-Dithiahexane 2,5-Dioxide

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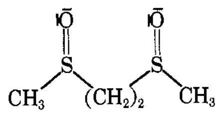
A number of coordination compounds of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) with transition metal salts have been synthesized, and their structures were determined by chemical analyses, infrared spectra, electronic absorption spectra, X-ray diffraction patterns, and magnetic susceptibility measurements. Compounds containing the complex cations $[M(DTHO_2)_3]^{2+}$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+}) and the compounds $[Pd(DTHO_2)Cl_2]$ and $[Pt(DTHO_2)Cl_2]$ are reported.

Introduction

Dimethyl sulfoxide (DMSO) is known to form coordination compounds with several metal ions. Their preparation, properties, and various physical characteristics have been reported.[2–7] The present paper describes the results of a similar study on the compounds of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) with some metals of the transition series, namely, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, and Pt^{2+}, as well as Zn^{2+} and Cd^{2+}. In all of the known metal complexes of DMSO except Pd^{2+} and Pt^{2+}, coordination takes place through the oxygen atom, and the same was to be expected for $DTHO_2$. The bidentate ligand, $DTHO_2$, whose structure is best represented by I and II, can form a seven-membered ring around a single metal ion.[8,9]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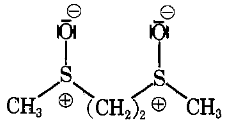
II

Because there are no known reports describing the donor properties of $DTHO_2$ and its complexes with metal ions, we undertook this study. Upon examination of the magnetic and spectral properties of the complexes of the transition metals, one concludes that the compounds are quite similar to DMSO complexes. The bidentate nature of the ligand is confirmed, and, as would be expected, $DTHO_2$ gives rise to a stronger ligand field than that of DMSO. Since the ligand has two equivalent asymmetric sulfur atoms, it exists in *dl* and *meso* modifications. Conclusive evidence is not available to indicate whether the high-melting (α) modification used in this work is the internally compensated *meso* isomer or the racemic *dl* mixture. Tris-chelate complexes of either the *meso* or *dl* form of $DTHO_2$ could occur as two pairs of optical enantiomorphs. The problem of separation and resolution of stereoisomers will be left for future investigation.

Experimental Section

All materials were of at least reagent grade. The compound 2,5-dithiahexane (DTH) was obtained from Aldrich Chemicals and was used in the preparation of $DTHO_2$ without further purification.

Analytical Procedures.—Perchlorates were determined by precipitation with nitron.[10] Carbon, hydrogen, and chloride analyses were performed by Weiler and Strauss, Microanalytical Laboratory, Oxford, England. Metal analyses were determined by EDTA titration.[11]

Preparation of Compounds.—The ligand $DTHO_2$ was synthesized from DTH. The α isomer, mp 166° (lit.[12] 164°), prepared by a method to be reported,[13] was used in this investigation.

Unless otherwise indicated, all complexes of $DTHO_2$ were prepared as follows.

Cobalt(II) perchlorate hexahydrate, $Co(ClO_4)_2 \cdot 6H_2O$ (0.732 g, 0.002 mole), was dissolved in 5 ml of methanol. To this solution was added $DTHO_2$ (0.924 g, 0.006 mole) dissolved in 15 ml of methanol. Immediate precipitation of a rose-pink crystalline material occurred after mixing the two solutions. The product

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[1] Undergraduate Research Participant, Summer, 1966.

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Table I

Analytical and Other Data of 2,5-Dithiahexane 2,5-Dioxide Complexes

		Analyses, %							
		Theory				Found			
Compound	Color	C	H	ClO_4	M	C	H	ClO_4	M
$Mn(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Colorless	20.11	4.22	27.76	7.67	20.26	4.27	27.12	7.59
$Fe(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Yellow	20.09	4.22	27.72	...	20.27	4.56	27.63	...
$Co(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Rose-pink	20.00	4.20	27.60	8.18	20.08	4.56	27.59	8.10
$Ni(C_4H_{10}S_2O_2)_3(ClO_4)_2$[a]	Light green	20.01	4.20	27.61	8.15	20.53	4.38	26.71	8.16
$Cu(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Light blue	19.87	4.17	27.43	8.76	20.13	4.63	27.56	8.84
$Zn(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Colorless	19.82	4.16	27.36	8.99	19.70	4.04	27.20	9.05
$Cd(C_4H_{10}S_2O_2)_3(ClO_4)_2$	Colorless	18.62	3.91	25.70	...	18.61	4.16	25.35	...
$Pd(C_4H_{10}S_2O_2)Cl_2$[b]	Yellow	14.49	3.04	...	...	14.28	3.53	...	...
$Pt(C_4H_{10}S_2O_2)Cl_2$[c]	Colorless	11.43	2.40	...	...	11.48	2.56	...	...

[a] Slightly hygroscopic. [b] Theory: Cl, 21.38. Found Cl, 21.31. [c] Theory Cl, 16.87. Found Cl, 16.78.

was filtered and washed several times with warm methanol to remove unreacted starting materials and then washed with ether. The crystalline product was dried *in vacuo* over P_4O_{10} at 80°; yield, 90%.

Identical procedures produced tris(2,5-dithiahexane 2,5-dioxide) crystalline complexes of Mn(II), Fe(II), Ni(II), Cu(II), Zn(II), and Cd(II) perchlorates in nearly quantitative yields (80–90%). These complexes decomposed violently at 170–185°.

Dichloro(2,5-dithiahexane 2,5-dioxide)palladium(II).—Palladium(II) chloride (0.267 g, 0.0015 mole) was dissolved in 100 ml of 1:1 hydrochloric acid. To this solution was added $DTHO_2$ (0.233 g, 0.0015 mole) dissolved in 20 ml of water. Immediate precipitation of a yellow microcrystalline solid occurred after mixing the two solutions. The product was filtered and washed with methanol and ether. The material was dried for 1 hr *in vacuo* over P_4O_{10}; yield, 66%. The yellow material decomposed to a dark brown solid at 194°.

Dichloro(2,5-dithiahexane 2,5-dioxide)platinum(II).—Potassium tetrachloroplatinate(II) (0.580 g, 0.0014 mole) was dissolved in water to give an orange solution. An aqueous solution of $DTHO_2$ (0.220 g, 0.0014 mole) was added. After gentle heating for 15 min, a white crystalline product separated and the solution became colorless. This product was filtered and washed with methanol and ether and dried *in vacuo* over P_4O_{10}; yield, 75%; dec pt 242°.

Physical Measurements.—Infrared spectra were obtained as Nujol mulls in the 4000–250-cm^{-1} region using a Perkin-Elmer 521 recording spectrophotometer. The spectra were frequency calibrated with a polystyrene film. Electronic absorption spectra in the visible and near-infrared regions of solutions and Nujol mulls[14] were obtained by using a Cary Model 14 recording spectrophotometer. The reflectance spectra in the visible region were obtained with a Beckman DU spectrophotometer equipped with a reflectance attachment. USP magnesium carbonate was used as a reference standard.

Magnetic susceptibilities were obtained on a Faraday balance which had been calibrated with mercury(II) tetrathiocyanatocobaltate(II).[15] Molar susceptibilities were corrected for diamagnetism.[16] Magnetic moments were calculated using $\mu = 2.84\sqrt{\chi_M^{cor}T}$.

X-Ray diffraction patterns were obtained using a General Electric Model XRD-5 unit and a direct recording diffractometer. Nickel-filtered copper radiation was employed. The compounds were ground in a mortar and packed into a sample holder. Relative intensities were estimated according to relative peak heights. Several compounds were analyzed two or more times after repacking to check for preferential orientation. The relative intensities were found to be fairly constant after repacking.

Discussion

General and X-Ray Diffraction Studies.—Perhaps the most striking feature of all of the complexes prepared in this study is the lack of water of any kind in their formulation. None of the infrared spectra contains bands associated with water, coordinated or otherwise, yet almost all complexes were obtained by using hydrated salts as starting materials. Results of analyses of the complexes conform to the formulas $[M(DTHO_2)_3](ClO_4)_2$, where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} and $[M(DTHO_2)Cl_2]$, where M = Pd^{2+} and Pt^{2+} (Table I).

X-Ray diffraction patterns of $[M(DTHO_2)_3](ClO_4)_2$ complexes are very similar in *d* (Å) values and intensities. This suggests that isomorphism exists among all these compounds. The X-ray diffraction patterns for $[Pd(DTHO_2)Cl_2]$ and $[Pt(DTHO_2)Cl_2]$ exhibit very poor resolution with much overlapping in the patterns, but they are very similar to each other and different from the $[M(DTHO_2)_3](ClO_4)_2$ complexes.

Magnetic Susceptibility Studies.—The magnetic moments of the $DTHO_2$ complexes in Table II are in the expected range for octahedral high-spin manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) complexes.[17] The magnetic moment of the octahedral cobalt(II) $DTHO_2$ complex falls in the expected range of 4.9–5.2 BM. The values of octahedral cobalt(II) dimethyl sulfoxide[2] and tetramethylene sulfoxide[18] complexes are also within this range. Octahedral cobalt(II) complexes generally exhibit magnetic moments much higher than the spin-only value of 3.9 BM be-

Table II

Magnetic Properties of 2,5-Dithiahexane 2,5-Dioxide Complexes

Compound	$10^6\chi_g$	$10^6\chi_M$	$10^6\chi_M^{cor}$	μ_{eff},[a,b] BM
$[Co(DTHO_2)_3](ClO_4)_2$	14.65	10,548	10,881	5.11
$[Ni(DTHO_2)_3](ClO_4)_2$	6.15	4,428	4,761	3.37
$[Mn(DTHO_2)_3](ClO_4)_2$	20.98	15,021	15,355	6.07
$[Fe(DTHO_2)_3](ClO_4)_2$	17.00	12,155	12,488	5.51
$[Cu(DTHO_2)_3](ClO_4)_2$	2.08	1,506	1,839	2.10

[a] Values reported are for 300°K. [b] $\mu_{eff} = 2.84\sqrt{\chi_M^{cor}T}$ BM, average of two determinations.

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[17] B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 278.

[18] R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

cause of orbital contributions from the $^4T_{1g}$(F) ground state and the ^{4}T excited states.[17]

The nickel(II) DTHO$_2$ complex exhibits a magnetic moment value of 3.37 BM which is in agreement with O$_h$ symmetry. This compares to hexakis(dimethyl sulfoxide)nickel(II) perchlorate which has a value of 3.4 BM.[2] The spin-only value of 2.8 BM for nickel(II) complexes is seldom exceeded by more than 0.7 BM. This has been examined by considering that orbital contributions cannot arise from the $^3A_{2g}$ ground state but only from the ^{3}T excited state.[17]

The tris(2,5-dithiahexane 2,5-dioxide)manganese(II) perchlorate complex exhibits a magnetic moment of 6.07 BM. This value differs only slightly from the spin-only value of 5.9 BM because no orbital contribution occurs in the $^4A_{1g}$ ground state and because there are no excited states with a multiplicity of six.[17]

The iron(II) and copper(II) DTHO$_2$ complexes, as expected for six-coordinate species, show magnetic moment values of 5.51 and 2.10 BM, respectively.

Infrared Spectral Studies.—Figures 1 and 2 give representative examples of each type of infrared spectrum of the DTHO$_2$ complexes, along with the spectrum of the free ligand. Only the S–O, C–S, and metal–ligand vibrational frequencies, along with some other important vibrational frequencies, will be considered in detail. Infrared measurements in the 4000–1200-cm^{-1} region were also studied but are not reported. The purpose for investigating this range is to demonstrate the absence of water.

In the case of [M(DTHO$_2$)$_3$](ClO$_4$)$_2$ (where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}), two bands were found to occur at nearly constant frequencies in the spectra of these complexes. The absorption was found to be rather broad and intense, occurring in the region 1070–1110 cm^{-1}. The second absorption, occurring at 625 cm^{-1}, was sharp but considerably less intense than the band found in the range 1070–1110 cm^{-1}. Wickenden and Krause[19] report similar bands for a nickel(II) acetonitrile perchlorate complex and have assigned these bands to the perchlorate anion. The absence of any splitting of the broad band in the region 1070–1110 cm^{-1} would seem to eliminate the possiblity of perchlorate coordination in the DTHO$_2$ complexes.

The S–O stretching vibrational frequency of the uncomplexed DTHO$_2$ occurs in the range 1015–1055 cm^{-1}. This range is found for mull spectra, KBr pellets, and also spectra in chloroform solution. The values of our work are in close agreement with those reported by Cairns and coworkers.[20] These workers assign the S–O stretching frequency to a range of 1045–1055 cm^{-1} in solution with a reduction to 1017–1035 cm^{-1} in the mull, while we find a reduction to 1015–1022 cm^{-1} in the mull.

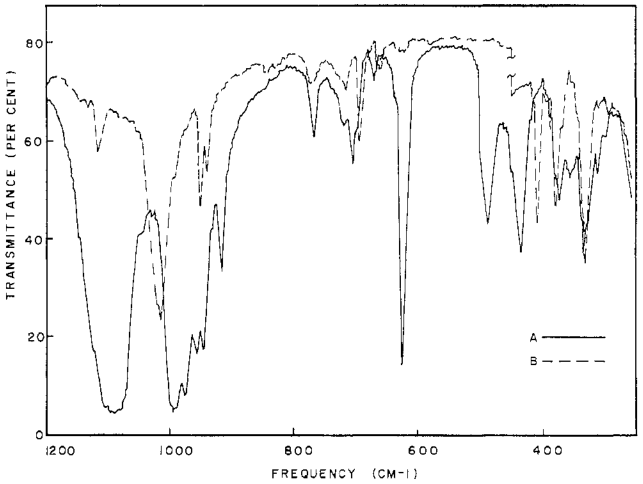

Figure 1.—Infrared spectra of (A) [Co(DTHO$_2$)$_3$](ClO$_4$)$_2$ (——) and (B) DTHO$_2$, 2,5-dithiahexane 2,5-dioxide (- - - -).

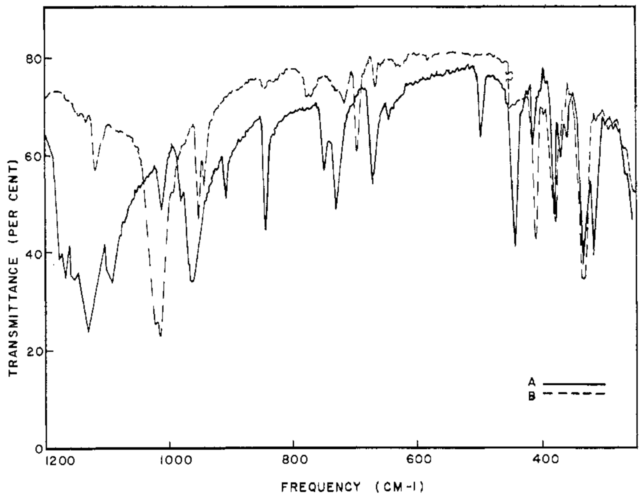

Figure 2.—Infrared spectra of (A) [Pt(DTHO$_2$)Cl$_2$] (——) and (B) DTHO$_2$, 2,5-dithiahexane 2,5-dioxide (- - - -).

It has been reported[3,4,21] that it is possible to determine from $\Delta\nu$(SO) [ν(SO)(ligand) $-$ ν(SO)(complex)] whether coordination in sulfoxide complexes occurs *via* the oxygen or the sulfur atom. This idea has very recently received direct support from the work of Bennett, Cotton, and Weaver.[22] Their X-ray investigation of an iron(II) complex and a palladium(II) complex with DMSO definitely confirms that O- and S-bonded complexes of DMSO are formed, respectively, as predicted from infrared spectra. From infrared data it can be concluded that in all of the first-row transition metal [Mn(II) through Zn(II)] and Cd(II) complexes, the frequency shift upon complexation of the DTHO$_2$ was toward lower frequency values. The magnitude of this shift ranges from 22 to 40 cm^{-1}. It is therefore concluded from the direction of the S–O shift that in all of these complexes studied, with the exception of Pd(II) and Pt(II) complexes, coordination occurs through the oxygen atoms of the DTHO$_2$. In the case of Pd(II) and Pt(II) DTHO$_2$ complexes, the shift toward higher frequency values ($\sim$77–108 cm^{-1}) would appear to rule out coordination through oxygen and suggests that sulfur coordination is occurring, possibly by forming a

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TABLE III

NEAR-INFRARED AND VISIBLE SPECTRA OF SOME 2,5-DITHIAHEXANE 2,5-DIOXIDE COMPLEXES

Compound	Assignment	Nujol mull, max, cm^{-1}	80% ethanol (with excess $DTHO_2$) soln, max, cm^{-1}	ϵ_{max}, l. mole^{-1} cm^{-1}
$[Co(DTHO_2)_3](ClO_4)_2$	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$	8,300	8,000	1.60
		(16,800)[a]	(17,000-16,000)[a]	(2.00)
	$\longrightarrow {}^4A_{2g}(F)$	19,000	18,700	5.6
		20,500[b]		
	$\longrightarrow {}^4T_{1g}(P)$	21,400[b]	20,100[b]	4.6
$[Ni(DTHO_2)_3](ClO_4)_2$	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$	8,400[b]	8,600	2.7
		13,100	12,900[b]	3.0
	$\longrightarrow {}^3T_{1g}(F)$	14,900	15,000	2.7
	$\longrightarrow {}^3T_{1g}(P)$	20,800[a]	25,100	6.6
		24,400		
$[Cu(DTHO_2)_3](ClO_4)_2$	$^2E_g \longrightarrow {}^2T_{2g}$	12,400[c]	12,200[c]	60.0
$[Fe(DTHO_2)_3](ClO_4)_2$	$^5T_{2g} \longrightarrow {}^5E_g(D)$	10,600	10,300	45.0

[a] Very broad shoulder, value given is an estimate. [b] Shoulder. [c] Broad unsymmetrical absorption.

five-membered chelate around these metals. The suggestion that the donor atom is sulfur in the Pd(II) and Pt(II) complexes is in agreement with the conclusions of Bennett and coworkers,[22] based on X-ray data for the Pd(II) DMSO complex.

The S–O stretching spectrum for the solid, uncoordinated $DTHO_2$ with strong absorption at 1015 and 1022 cm^{-1} is remarkably similar to that of *trans*-1,4-dithiane 1,4-dioxide.[20] The latter substance has a diaxial chair conformation, confirmed by X-ray data. The marked similarity of the two spectra suggests that $DTHO_2$ molecules in the crystalline state, despite their open chain, may assume a similar configuration with two independent and nearly equivalent S–O groups. The chloroform solution of $DTHO_2$ has strong absorption with two distinct bands at ~1020 and 1060 cm^{-1}, in contrast with the chloroform solution of the *trans* cyclic disulfoxide which has a single narrow band at ~1055 cm^{-1}. The difference is presumably due to relatively free bond rotation in the solution of $DTHO_2$.[20] In the complexes the SO stretching vibrational bands of $DTHO_2$ shift to substantially lower frequencies (except in the case of Pt(II) and Pd(II)) and appear as an intense band with splitting.

The bands in the region 665–719 cm^{-1} for $DTHO_2$ are assigned to the C–S stretching vibration, based on Bellamy's assignment for DMSO.[23] Selbin, *et al.*,[5] have assigned a value of 697 cm^{-1} for the C–S stretching vibrational band of DMSO and a range of 707–737 cm^{-1} for the band upon coordination. The shift to 704–770 cm^{-1} for the $DTHO_2$ complexes is consistent with the above findings.

Two strong bands which are not observed in the free $DTHO_2$ appear in the region 420–490 cm^{-1} in all of these complexes (Figures 1 and 2). We tentatively attribute the stong peak in the lower frequency region (~420 cm^{-1}) to the $M \leftarrow DTHO_2$ bond. This assignment is consistent with the value reported by Berney and Weber[24] for the metal–oxygen stretching vibration for the divalent transition metal complexes of DMSO. The frequency order in the $DTHO_2$ complexes is the same as reported for DMSO complexes:[24] Ni(II) > Co(II) > Zn(II) > Fe(II) > Mn(II) ≃ Cu(II) ≃ Cd(II).

$PdCl_2 \cdot DTHO_2$ and $PtCl_2 \cdot DTHO_2$.—The infrared spectral data in the regions 500–250 and 1200–500 cm^{-1} are shown in Figure 2. Assignments have been made for the ν(M–Cl) and ν(M–L) modes, although the latter (Pd–L, 430 cm^{-1}; Pt–L, 445 cm^{-1}) are regarded as tentative and probably involve only partial metal–ligand stretching character. In accordance with Adams, *et al.*,[25] two ν(Pt–Cl) bands are expected below 400 cm^{-1} and those at 335 and 318 cm^{-1} are accordingly assigned to these modes. For $PdCl_2 \cdot DTHO_2$, 330 and 322 cm^{-1} may be assigned to the ν(Pd–Cl) bonds.

Visible and Near-Infrared Spectral Studies.—The spectra obtained for solutions and Nujol mulls of these complexes are given in Table III. A comparison of the spectra in the solution state and the solid state indicates that the primary absorbing species in solution is the same as in the solid. The spectra of the cobalt(II) and nickel(II) compounds are typical of O_h symmetry. Therefore, assignments of the observed absorption bands were made on the basis of octahedral configuration. Using the secular equations of Orgel[26] and the energy of the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition, a value of 14,780 cm^{-1} was calculated for the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition of tris(2,5-dithiahexane 2,5-dioxide)nickel(II) perchlorate. This value compares favorably with the experimental value of 15,000 cm^{-1} (Table III). The value $E(P) - E(F)$ was also calculated for the $[Co(DTHO_2)_3](ClO_4)_2$ and $[Ni(DTHO_2)_3](ClO_4)_2$ complexes (Table IV). In the case of cobalt(II) the values of Dq and β were calculated on the basis of O_h symmetry. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition could not be resolved but appeared as a broad shoulder on the 18,700-cm^{-1} peak. This transition, which involves two electrons, would be expected to be of very weak intensity.[27] The nickel(II) Dq value of 860 cm^{-1} places $DTHO_2$ in the spectrochemical series near water. Since 2,5-dithia-

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[23] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 353.

[24] C. V. Berney and J. H. Weber, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-86.

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[27] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 256.

TABLE IV

LIGAND FIELD PARAMETERS[a] OF THE 2,5-DITHIAHEXANE 2,5-DIOXIDE COMPLEXES

Compound	Dq, cm^{-1}	$E(P) - E(F)$, cm^{-1}	β^b
$[Co(DTHO_2)_3](ClO_4)_2$	900	12,000	0.81
$[Ni(DTHO_2)_3](ClO_4)_2$	860	12,820	0.87
$[Fe(DTHO_2)_3](ClO_4)_2$	1030	...	...

[a] A description of the procedure which was followed in calculating ligand field parameters is given by J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *Inorg. Chem.*, **4**, 18 (1965). [b] The quantity β is defined as the ratio B'/B where B' is the P–F term splitting for the complex and B the value for the gaseous ion with no crystalline field.

hexane 2,5-dioxide is a bidentate ligand, it gives larger Dq values than do other sulfoxides.[28] This may be attributed to chelation. The chelate effect is demonstrated by comparing the Dq values for nickel(II) perchlorate complexes of various monodentate ligands and similar bidentate ligands: pyridine (1010 cm^{-1})[29] *vs.* 2,2-bipyridine (1150 cm^{-1}),[30] pyridine N-oxide (840 cm^{-1})[28] *vs.* 2,2-bipyridine 1,1′-dioxide (857 cm^{-1}),[4] methylamine (993 cm^{-1})[31] *vs.* ethylenediamine (1150 cm^{-1}),[32] and N,N-dimethylacetamide (769 cm^{-1})[33] *vs.* N,N,-N′N′-tetramethylmalonamide (860 cm^{-1}).[34] 2,4-Dithiahexane 2,5-dioxide (860 cm^{-1}) may thus be compared with dimethyl sulfoxide (773 cm^{-1})[28] or tetramethylene sulfoxide (775 cm^{-1}).[28] On this basis we conclude that there is chelation. Furthermore, the Dq value for the five-membered ring chelate complex of 2,5-dithiahexane with nickel(II) ion (1060 cm^{-1})[35] is considerably greater than that of the seven-membered chelate of $DTHO_2$ with nickel(II) (860 cm^{-1}). A similar trend has previously been reported[8] for tris(2,2-bipyridine)nickel(II) ion (with five-membered rings, Dq = 1150 cm^{-1}) and tris(2,2-bipyridine 1,1′-dioxide)nickel(II) ion (with seven-membered rings, Dq = 857 cm^{-1}). Therefore, it is quite reasonable to conclude that chelate complexes with seven-membered rings around nickel(II) ion are generally less stable than those with five-membered rings.

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Multidentate Coordination Compounds. Chelating Properties of Aliphatic Amines Containing α-Pyridyl Residues and Other Aromatic Ring Systems as Donor Groups[1-3]

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A series of multidentate polyamines containing α-pyridyl residues or other aromatic ring systems as donor groups were synthesized and their affinity for divalent transition metal ions investigated. The substances prepared are 2,6-dimethylenebis-(N-2-picolylamino)pyridine, di(2-picolyl)amine, N,N′-bis(2-picolyl)ethylenediamine, N,N′-bis(4-(5)-imidazolylmethyl)-ethylenediamine, N,N′-bis(*o*-aminobenzyl)ethylenediamine, and N,N′-bis(*o*-hydroxybenzyl)ethylenediamine. The proton association constants of the ligands and the stability constants of the Zn(II), Co(II), and Ni(II) chelates were determined by pH titrations at 25° in 0.1 M KCl. The formation constants for Cu(II) with 2,6-dimethylenebis(N-2-picolylamino)pyridine, N,N′-bis(4-(5)-imidazolylmethyl)ethylenediamine, and N,N′-bis(*o*-hydroxybenzyl)ethylenediamine were determined also.

Introduction

Metal chelates of Schiff bases derived from pyridine-2-aldehyde and other *ortho*-substituted aromatic aldehydes and various aliphatic amines have been the subject of intensive research not only because of their interesting stereochemical properties[5] but also because of their usefulness as model systems in the study of enzymatic reactions.[6]

Quite in contrast, the metal complexes of the closely related saturated amine compounds (the latter are easily obtainable by hydrogenation of the aldimines) have received relatively little attention. While some of the relevant work has dealt with the configurational

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(1) This work is described in more detail in the Diplom Thesis (Universitat Tubingen, 1961) and Ph.D. Thesis (Universitat Tubingen, 1963) by Dieter W. Gruenwedel.

(2) Material supplementary to this article has been deposited as Document No. 9786 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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