$[HgI(CN)]^2/[HgI_2][Hg(CN)_2]$. From the solubility of HgI_2 measured in 0.4 M $Hg(CN)_2$, we compute K = 0.14. The concentration of the species HgI_2 is assumed to be equal to 1.05×10^{-4} M, the measured solubility in water. From the spectra of Figure 4 we compute K = 0.13. The spectra labeled 0 and 0.1 M $Hg(CN)_2$ are taken to be those of the species HgI_2 and $HgI(CN)$, respectively. Beck and Gazier[10] report that K = 0.2 in dioxane and 0.11 in water.

Conclusions

The following picture appears consistent with both the ultraviolet and Raman results: (1) At low CN^- concentrations, but in concentrated NaI, tetrahedral HgI_4^{2-} reacts to give the mixed complex, $Hg(CN)I_3^{2-}$, of likely C_{3v} symmetry. (2) At slightly higher CN^- concentrations (and well before formation of $Hg(CN)I_3^{2-}$ is complete), formation of a dicyanide complex with a linear $Hg(CN)_2$ group becomes dominant, with iodides bound in equatorial positions. (3) These dicyanide complexes are still present at free CN^- concentrations of a few tenths molar, but $Hg(CN)_3I^{2-}$ predominates.

The results of this study provide no quantitative estimate for the number of iodide ions which are bound in mixed-ligand dicyanide complexes. Coordination with iodide in solid $KI \cdot Hg(CN)_2$ gives an equatorial ring of four iodides. It seems plausible, from stoichiometric considerations and from the fact that "free" $Hg(CN)_2$ is not observed, that the number of bound iodides in solution is <4 for the species we have designated $Hg(CN)_2I_x^{x-}$, in all but perhaps the most concentrated NaI solutions.

Monomeric $HgI(CN)$ is formed when HgI_2 is dissolved in aqueous $Hg(CN)_2$ solutions.

Acknowledgments.—Professor John C. Bailar, Jr., provided helpful suggestions both for the experimental design and the interpretation of the results. Crystallographic properties of $NaI \cdot Hg(CN)_2 \cdot 2H_2O$ were determined by Professor A. Rosenzweig.

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(10) M. T. Beck and F. Gazier, *J. Inorg. Nucl. Chem.*, **26**, 1755 (1964).

Contribution from the Istituto di Chimica Generale e Inorganica,
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Four- and Five-Coordinated Complexes of Cobalt(II) and Nickel(II) with Tridentate Schiff Bases

By L. Sacconi and I. Bertini

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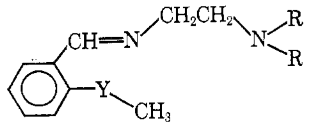
The Schiff bases derived from *o*-methoxybenzaldehyde (MOB) and N,N-dialkylethylenediamines ($MOBenNR_2$) and N,N-dialkyltrimethylenediamines ($MOBtnNR_2$) (both with the potential set of donor atoms ONN), or ethylenediamine ($(MOB)_2en$) and 1,2-propylenediamine ($(MOB)_2pn$) (both with the potential set of donor atoms ONNO), form adducts with cobalt(II) and nickel(II) salts of the general formula MLX_2. All of the complexes are of the high-spin type. The cobalt complexes are pseudo-tetrahedral. The nickel ones are five coordinated or pseudo-tetrahedral depending on the nature of the R substituent. The nickel complexes in solution with inert solvents often give rise to equilibria between the two species.

Introduction

After the recent discovery in this laboratory of some pentacoordinate, high-spin, Schiff-base complexes of nickel(II)[1,2] and cobalt(II),[2,3] a systematic study of this type of compound has been undertaken with the purpose of extending the available information on pentacoordinate complexes.

It has been found that the tridentate ligand $MABenNEt_2$ (I, Y = NH, R = C_2H_5) is particularly well suited to form high-spin pentacoordinate complexes with cobalt(II) and nickel(II) salts of the formula MLX_2.[4] In this instance the donor atom set is NNN. It is quite general to find that high-spin pentacoordinate complexes are formed with ligands containing nitrogen and/or oxygen donor atoms.[5] When the donor atoms are phosphorus or arsenic atoms, the pentacoordinate complexes formed are of the low-spin type.[6]



I

The ligand $MSBenNEt_2$ (I, Y = S, R = C_2H_5) has a donor atom set SNN and it too forms high-spin pen-

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(1) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(2) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **87**, 3102 (1965); L. Sacconi and I. Bertini, *ibid.*, **88**, 5182 (1966).

(3) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(4) L. Sacconi, I. Bertini, and R. Morassi, *ibid.*, **6**, 1548 (1967).

(5) (a) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966); (b) J. Lewis, R. S. Nyholm, and S. A. Rodley, *Nature*, **207**, 72 (1965); M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); **6**, 445 (1967); M. Ciampolini and J. Gelsomini, *ibid.*, **6**, 1821 (1967); Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966); F. Lions, J. G. Dance, and J. Lewis, *J. Chem. Soc., A*, 565 (1967); S. M. Nelson and J. Rodgers, *Inorg. Chem.*, **6**, 1390 (1967).

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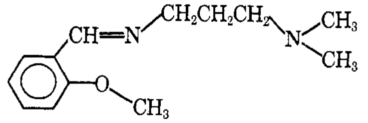
tacoordinate complexes with nickel (II).[7] By contrast with cobalt(II) it forms only tetrahedral complexes.[7] It therefore appeared interesting to see what kind of complexes might be formed by nickel(II) and cobalt(II) with the ligands MOBenNR_2 (I, Y = O) and MoBtnNMe_2 (II) in which the donor set is ONN. It was also convenient to study the tetradentate ligands $(\text{MOB})_2\text{en}$ (III, $R' = H$) and $(\text{MOB})_2\text{pn}$ (III, $R' = CH_3$) at the same time, and to compare the results with those obtained from the ligands BenNEt_2 (IV) and B_2pn (V). Complexes with the general formula MLX_2 have been obtained with all of these ligands.



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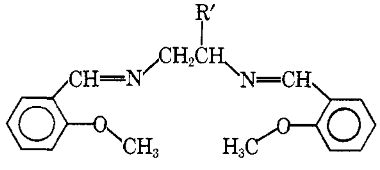

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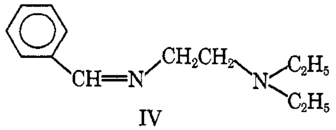

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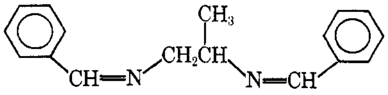

V

Experimental Section

Preparation of the Ligands.—The salicylaldehyde was methylated using dimethyl sulfate as reported in the literature.[8] The *o*-methoxybenzaldehyde obtained or benzaldehyde was refluxed for 0.5 hr with a stoichiometric amount of the appropriate amine. The compounds were crystallized from chloroform–petroleum ether (bp 40–70°) for the solid $(\text{MOB})_2$ and B_2 derivatives. The other liquid derivatives were dried over Na_2SO_4 after the addition of some ether and then distilled under vacuum (0.3–0.5 mm). All of the ligands were used in the preparation of the complexes without any further purification.

Preparation of the Complexes.—All of the complexes were prepared by the same general method. A solution of 10 mmol of the crude ligand dissolved in 20 ml of dry *n*-butyl alcohol was added slowly to a hot solution of 10 mmol of the appropriate metal salt in 50 ml of *n*-butyl alcohol. After boiling for some minutes, the solution was filtered and concentrated, and generally crystals were obtained. In some cases cyclohexane was added to promote crystallization. The crystals were collected by filtration and dried in a stream of dry nitrogen. The analytical data and melting or decomposition temperatures are given in Table I.

Physical Measurements.—The apparatus and experimental technique used for the magnetic measurements are described in a previous paper.[9] The Gouy tube was calibrated with freshly distilled water and $\text{Hg(Co(NCS)}_4)$.[10] The magnetic data are reported in Table II. Absorption spectra were recorded in the range 5000–25,000 cm^{-1} with a Beckman DK-2 spectrophotometer using 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. The absorption maxima and molar absorbancies are given in Table III. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer employing mulls in Nujol supported on CsBr plates. The spectra show a strong absorption band in the range 1600–1650 cm^{-1}, assigned to the C=N stretching vibration. The value of the molar conductivity and of the degree of association for a *ca.* 10^{-3} M solution in 1,2-dichloroethane of $\text{Ni(MOBenNEt}_2\text{)Br}_2$, determined as reported in ref 4, are: $\Lambda_M = 0.8$ ohm^{-1} cm^2 M^{-1}; $n = 0.93$.

Results and Discussion

$\text{Ni(MOBenNEt}_2\text{)X}_2$.—These complexes form purple crystals which are moisture sensitive. They dissolve in polar organic solvents such as nitro or chloro derivatives. The magnetic moments vary from 3.30 to 3.50 BM. Molecular weight and conductivity measurements taken on $\text{Ni(MOBenNEt}_2\text{)Br}_2$ in solution indicate that this complex is monomeric. The electronic spectra of the chloride, bromide, and iodide complexes are very similar to each other, showing only slight frequency shifts which can be correlated with the position of the halogen in the spectrochemical series. The diffuse reflectance spectra, which are practically identical with the absorption spectra, show two strong bands at 10,000 and 18,000 cm^{-1} with shoulders at 8000 and 11,000 cm^{-1}. These results, taken together with the close similarity of the spectra with those for

TABLE I

ANALYTICAL DATA FOR THE NICKEL(II) AND COBALT(II) COMPLEXES

		% N		% metal	
Compound	Mp, °C	Calcd	Found	Calcd	Found
$\text{Ni(MOBenNEt}_2\text{)Cl}_2$[a]	186–189	7.70	7.82	16.12	16.06
$\text{Ni(MOBenNEt}_2\text{)Br}_2$	220–223	6.18	6.15	12.96	12.85
$\text{Ni(MOBenNEt}_2\text{)I}_2$	170–176	5.12	5.00	10.73	10.73
$\text{Ni(BenNEt}_2\text{)Br}_2$[b]	203–205	6.60	6.59	13.88	13.79
$\text{Ni(B}_2\text{pn)Br}_2$	238–240	5.98	5.98	12.52	12.86
$\text{Ni(MOBenNMe}_2\text{)Cl}_2$	184–187	8.33	8.46	17.47	17.43
$\text{Ni(MOBenNMe}_2\text{)Br}_2$[c]	178–182	6.59	6.40	13.81	13.77
$\text{Ni(MOBtnNMe}_2\text{)Cl}_2$	237–240	8.00	7.88	16.77	16.70
$\text{Ni(MOBtnNMe}_2\text{)Br}_2$	220–223	6.38	6.16	13.37	13.68
$\text{Ni((MOB)}_2\text{en)Cl}_2$	210 dec	6.57	6.52	13.78	13.90
$\text{Ni((MOB)}_2\text{en)Br}_2$	200 dec	5.45	5.70	11.40	11.31
$\text{Ni((MOB)}_2\text{pn)Cl}_2$	212–217	6.36	6.40	13.34	13.32
$\text{Ni((MOB)}_2\text{pn)Br}_2$	200–207	5.30	5.42	11.10	11.06
$\text{Co(MOBenNEt}_2\text{)Cl}_2$	204–206	7.70	7.62	16.12	15.99
$\text{Co(MOBenNEt}_2\text{)Br}_2$[d]	204–207	6.18	6.07	12.96	12.70
$\text{Co(MOBenNEt}_2\text{)I}_2$	186–189	5.12	5.54	10.74	10.50
$\text{Co(MOBtnNMe}_2\text{)Br}_2$	203–206	6.38	6.56	13.37	13.17

[a] Calcd: C, 46.23; H, 6.05. Found: C, 46.23; H, 6.15. [b] Calcd: C, 36.92; H, 4.74. Found: C, 36.88; H, 4.77. [c] Calcd: C, 33.92; H, 4.27. Found: C, 33.95; H, 4.46. [d] Calcd: C, 37.10; H, 4.86. Found: C, 37.00; H, 4.93.

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(7) L. Sacconi and G. P. Speroni, *Inorg. Chem.*, **7**, 295 (1968).

(8) A. Katshalowsky and St. v. Kostanecki, *Chem. Ber.*, **37**, 2346 (1904).

(9) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

TABLE II

MAGNETIC DATA FOR NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Temp, °C	$10^6\chi_g$, cgs units	$10^6\chi_M$, cgs units	μ_{eff}, BM
$Ni(BenNEt_2)Br_2$	20	10.47	4639	3.31
$Ni(B_2pn)Br_2$	20	9.23	4552	3.28
$Ni(MOBenNEt_2)Cl_2$	20	13.51	5160	3.48
$Ni(MOBenNEt_2)Br_2$	20	9.92	4729	3.34
$Ni(MOBenNEt_2)I_2$	19.5	8.12	4705	3.33
$Ni(MOBenNMe_2)Cl_2$	20	14.31	5002	3.44
$Ni(MOBenNMe_2)Br_2$	19	10.87	4830	3.38
$Ni(MOBtnNMe_2)Cl_2$	19.5	13.17	4836	3.38
$Ni(MOBtnNMe_2)Br_2$	19.5	10.46	4814	3.37
$Ni((MOB)_2en)Cl_2$	19	11.23	5008	3.44
$Ni((MOB)_2en)Br_2$	20	8.99	4876	3.40
$Ni((MOB)_2pn)Cl_2$	19.5	10.38	4804	3.37
$Ni((MOB)_2pn)Br_2$	19	8.51	4760	3.35
$Co(MOBenNEt_2)Cl_2$	20	22.91	8556	4.50
$Co(MOBenNEt_2)Br_2$	19.5	19.42	9033	4.61
$Co(MOBenNEt_2)I_2$	20	16.39	9229	4.67
$Co(MOBtnNMe_2)Br_2$	19.5	19.81	8923	4.59

TABLE III

SPECTROSCOPIC DATA FOR THE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Solvent	ν_{max}, cm^{-1} (ϵ)
$Ni(BenNEt_2)Br_2$		<5000, 6900, 10,200, 11,100 sh, 17,400 sh, 18,850
	$(CH_2Cl)_2$	7400 (21), 10,000 (84), 11,000 (56), 11,350 (50), 17,400 sh, 18,850 (196)
$Ni(B_2pn)Br_2$		<5000, 7500, 10,400, 11,500 sh, 18,700
	$(CH_2Cl)_2$	7400 sh, 10,200 (85), 11,200 (63), 11,400 (60), 18,700 (164)
$Ni(MOBenNEt_2)Cl_2$		<5000, 7150, 10,250, 11,400 sh, 16,100 sh, 19,200
	$C_2H_5NO_2$	8850 (21), 10,480 (42), 11,500 (35), 12,000 (33), 16,100 sh, 19,100 (94)
$Ni(MOBenNEt_2)Br_2$		7460 sh, 10,100, 16,600 sh, 19,040
	$C_2H_5NO_2$	7150 (24), 10,100 (70), 11,150 (55), 11,500 (41), 19,240 (124), 26,600 (229)
$Ni(MOBenNEt_2)I_2$		<5000, 7200 sh, 9750 sh, 10,600, 17,500
	$(CH_2Cl)_2$	7400 sh, 9700 (134), 10,500 (131), 17,800 (390)
$Ni(MOBenNMe_2)Cl_2$		7400, 11,100 sh, 13,350, 20,000 sh, 22,800
	$(CH_2Cl)_2$	8350 sh, 10,500 (30), 12,200 (35), 18,200 sh, 20,800 (75)
$Ni(MOBenNMe_2)Br_2$		5700, 8150 sh, 11,800, 18,200 sh, 20,800
	$(CH_2Cl)_2$	8340 sh, 10,530 sh, 11,630 (44), 20,400 (112)
$Ni(MOBtnNMe_2)Cl_2$		5700, 8500 sh, 11,900, 18,200 sh, 20,800
	$C_6H_5NO_2$	8000 (12), 10,800 sh, 12,200 (39), 18,200 sh, 20,800 (85)
$Ni(MOBtnNMe_2)Br_2$		5700, 8700 sh, 12,050, 17,900 sh, 20,000
	$C_6H_5NO_2$	8000 (17), 10,500 sh, 11,900 (58), 17,850 sh, 20,000 (140)
$Ni((MOB)_2en)Cl_2$		<5000, 7550, 10,250, 11,600 sh, 16,130 sh, 18,200 sh, 18,900
	$(CH_2Cl)_2$	8540 (26.3), 11,400 sh, 12,650 (34.1), 21,300 (36.1)
$Ni((MOB)_2en)Br_2$		<5000, 7500, 10,200, 11,100 sh, 18,500
	$(CH_2Cl)_2$	8500 (26), 11,100 sh, 12,650 (43), 21,300 (81)
$Ni((MOB)_2pn)Cl_2$		<5000, 7400, 10,500, 11,750 sh, 16,600 sh, 19,200
	$C_2H_5NO_2$	8150 (24), 11,100 (27), 12,500 (32), 21,000 (57)
$Ni((MOB)_2pn)Br_2$		<5000, 7450, 10,400, 11,500 sh, 18,900
	$C_2H_5NO_2$	8150 (22), 10,800 (34), 12,300 (43), 21,000 (85)
$Co(MOBenNEt_2)Cl_2$		6050, 7450, 10,200, 15,300, 15,600, 17,000
	$(CH_2Cl)_2$	6000 (34), 7450 (41), 10,300 (20), 15,400 (410), 15,750 (425), 17,150 (425)
$Co(MOBenNEt_2)Br_2$		6050, 7050, 10,000, 15,400, 16,600 sh, 17,300 sh
	$(CH_2Cl)_2$	6000 (41), 7150 (59), 9800 (35), 15,400 (870), 16,300 (720), 17,500 sh
$Co(MOBenNEt_2)I_2$		5700, 6700, 9250, 14,700, 17,100 sh
	$(CH_2Cl)_2$	5700 sh, 6700 (82), 9200 (52), 14,900 (720), 15,600 sh, 17,100 sh
$Co(MOBtnNMe_2)Br_2$		5900, 8000, 10,600, 15,400, 17,200 sh, 17,800 sh
		5900 (32), 7800 (56), 10,200 (46), 15,600 (580), 16,600 sh, 17,800 sh

the compounds $Ni((CH_3)_2NCH_2CH_2N(CH_3)_2)X_2$[11] (Figure 1) lead to the assignment of a donor atom set N_2X_2 and a distorted tetrahedral structure. This is confirmed by the fact that the spectra of the compound $Ni(BenNEt_2)Br_2$ derived from ligand IV are practically identical with those derived from ligand I (Y = O, R = C_2H_5) (Figure 1) showing that the methoxy group in the latter is not at all involved in the bonding. The magnetic moments are also in the range found for tetrahedral complexes of nickel(II).[12]

$Ni(MOBenNMe_2)X_2$ and $Ni(MOBtnNMe_2)X_2$.—These compounds are brick red and unstable to moisture, and they have magnetic moments of *ca.* 3.40 BM. The reflectance spectra are similar to those of the previous group of compounds, differing from them mainly in the values of the absorption frequencies (Figure 2). The two main peaks are found at 12,000–13,500 and 20,000–22,000 cm^{-1}. These frequencies cannot be reasonably assigned in terms of a tetrahedral structure because: (i) frequency shifts of 2000–3000 cm^{-1} compared with the previous group of compounds cannot be explained if the set of donor atoms is unchanged and (ii) a frequency of 12,000–13,500 cm^{-1} for the ν_2 transition would be higher than any found in known tetrahedral complexes of nickel(II).[13] On the other hand, the spectra are very similar to those of $Ni(MABenNEt_2)X_2$,[4] $Ni(MSBenNEt)_2X_2$,[7] $Ni(Me_5dien)X_2$[14] (Figure 2) which

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[11] L. Sacconi and I. Bertini, *Inorg. Nucl. Chem. Letters*, **2**, 29 (1966); L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).

[12] L. M. Venanzi, *et al.*, *J. Chem. Soc.*, 719 (1958); 2705, 4816 (1961), 693 (1962); F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961); L. Sacconi and J. Gelsomini, *Inorg. Chem.*, **7**, 291 (1968).

[13] K. Issleib and B. Mitscherling, *Z. Anorg. Allgem. Chem.*, **304**, 73 (1960); J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *ibid.*, **3**, 480, 671 (1964); W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, **47**, 1265 (1964); S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 3276 (1965).

[14] Me_5dien is $((CH_3)_2NCH_2CH_2)_2NCH_3$.[5a]

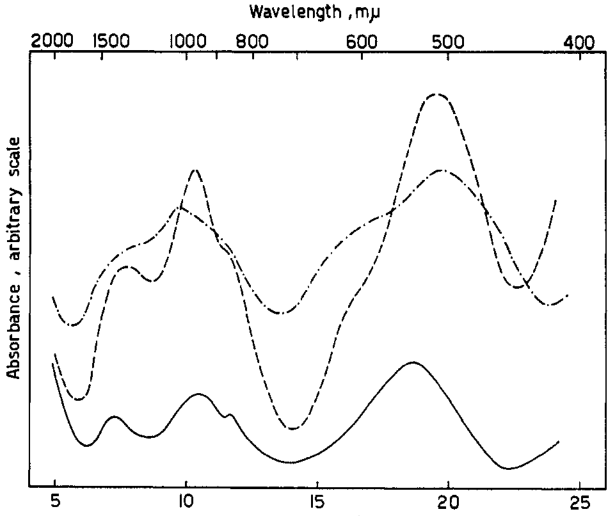


Figure 1.—Reflectance spectra of: $Ni(BenNEt_2)Br_2$, ———; $Ni(MOBenNEt_2)Cl_2$, — — —; $Ni((CH_3)_2NCH_2CH_2N(CH_3)_2)Br_2$, – · – · – ·.

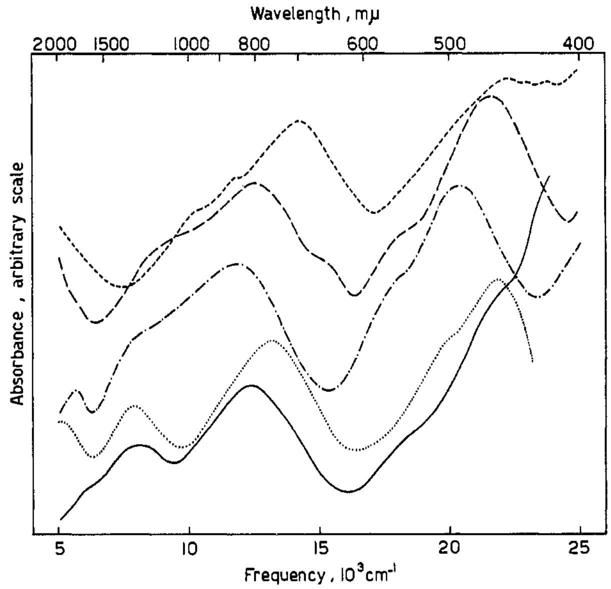
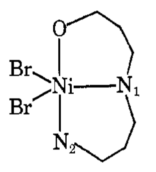


Figure 2.—Reflectance spectra of: $Ni(MABenNEt_2)Br_2$, ———; $Ni(MOBenNMe_2)Br_2$, – · – · – ·; $Ni(Me_5dien)Br_2$, — — —; $Ni(MSBenNEt_2)Br_2$, – – – –; $Ni(MOBH_2tnNHEt)Br_2$, · · · ·.

have been given a pentacoordinate structure and to that of $Ni(MOBH_2tnNHEt)Br_2$[15] (Figure 2) which has been found by X-ray analysis to be pentacoordinate. The stereochemistry of the last complex is intermediate between the square pyramid and the trigonal bipyramid with the angles N_2–Ni–O = 175.3° and Br–Ni–Br = 149.7°[15b]



This indicates that the oxygen atom in I (Y = O) occupies the fifth position about the central ion. The absorption frequencies of the peaks shift to lower frequencies on passing from the donor atom set SNN to NNN to ONN. However, this trend cannot be related to atom positions in the spectrochemical series because precise structural data are lacking. It can be noted that Jørgensen positions the ethereal sulfur between oxygen and nitrogen in the spectrochemical series.[16]

The spectra obtained in 1,2-dichloroethane or nitrobenzene solutions show some differences from those obtained with solids in that a broad band with at least two maxima between 10,000 and 13,000 cm^{-1} appears while the band in the visible region is shifted to lower frequencies. With increasing temperature the intensity of absorption at *ca.* 10,000 cm^{-1} increases while the band at *ca.* 13,000 cm^{-1} decreases in intensity and the band at *ca.* 20,000 cm^{-1} undergoes a red shift (Figure 3). This shows the presence of an equilibrium mixture between a tetrahedral species and a pentacoordinate species favoring the tetrahedral species at higher temperatures. Presumably it is the methoxy group which becomes detached from the metal atom. In this respect the behavior of the three ligands I (Y = NH, S, or O) is entirely similar.

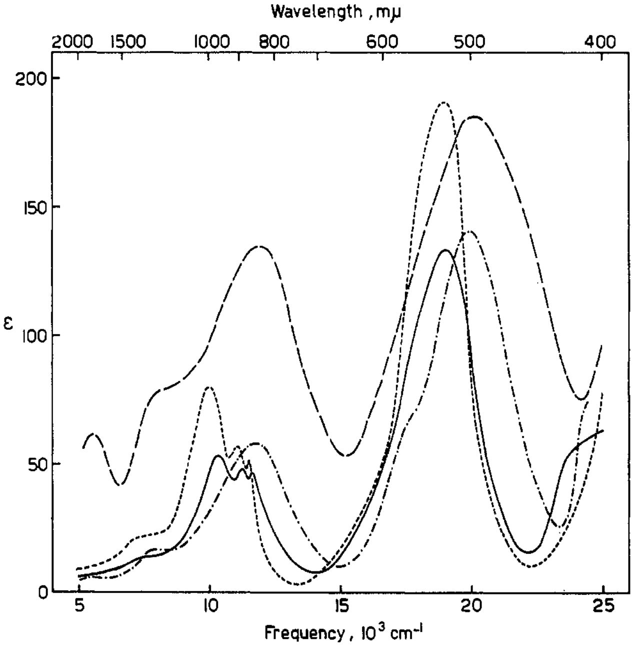


Figure 3.—Reflectance spectrum of $Ni(MOBtnNMe_2)Br_2$, — — —. Absorption spectra of: $Ni(BenNEt_2)Br_2$ in 1,2-dichloroethane, – – – –; $Ni(MOBtnNMe_2)Br_2$ in nitrobenzene at 20°, – · – · – ·, and at 120°, ———.

The fact that the $N(CH_3)_2$ derivatives are pentacoordinate while the $N(C_2H_5)_2$ derivatives are tetrahedral can be accounted for considering that the steric hindrance engendered by replacing the two methyl groups with ethyl groups will be sufficient to favor the formation of a tetrahedral structure.

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[15] (a) $MOBH_2tnNHEt$ is the dihydrogenated Schiff base obtained from *o*-methoxybenzaldehyde and N-ethyltrimethylenediamine ($CH_3OC_6H_4CH_2NHCH_2CH_2CH_2NH(C_2H_5)$); (b) P. L. Orioli and M. DiVaira, *J. Chem. Soc., A*, in press.

[16] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1972).

Ni((MOB)$_2$en)X$_2$ and Ni((MOB)$_2$pn)X$_2$.—These violet complexes are soluble in polar organic solvents. Their diffuse reflectance spectra are similar in form and absorption frequencies to those of the tetrahedral compounds reported here. They are moreover similar to those of the bidentate ligand B$_2$pn (V). This indicates that neither oxygen atom is bound to the metal. In solution the color changes to brown and a new absorption band appears at 12,000–13,000 cm^{-1} indicating that some pentacoordinate species are present in these solutions. With increasing temperature the proportion of the pentacoordinate species decreases (Figure 4).

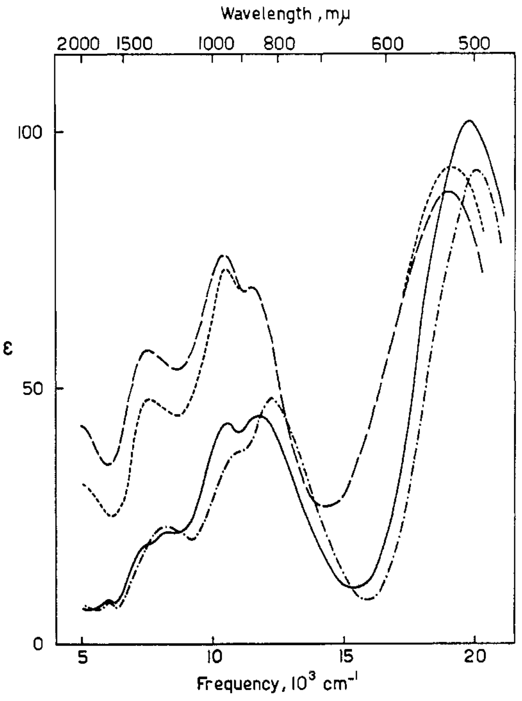

Figure 4.—Reflectance spectra of: Ni((MOB)$_2$pn)Br$_2$, — — —; Ni(B$_2$pn)Br$_2$, - - - -. Absorption spectra of Ni((MOB)$_2$pn)Br$_2$ in nitrobenzene: at 20°, - · - · - ·; at 120°, ———.

Thus in solution these compounds behave in much the same way as the pentacoordinate compounds described earlier (Figure 3). Even though the ligand contains four possible donor atoms, there is no evidence for the presence of any hexacoordinate species in solution. This is presumably due to the low donor power of the ethereal oxygen atoms.

As we have noted already, the spectra of the tetrahedral and pentacoordinate complexes reported here are very similar to each other in form and differ mainly in the absorption frequencies. The tetrahedral complex has at most a crystal field of point symmetry C_{2v}, so that all the crystal field terms of the nickel(II) ion are orbitally nondegenerate. The broad band at *ca.* 18,000 cm^{-1} which shows more than one maximum can be reasonably assigned to transitions to states arising from the free-ion term ^3P.[17] The band at *ca.* 10,000 cm^{-1} can be assigned to the transition to the highest level arising from the free-ion ^3F term, $^3A_2$, which correlates with the $^3A_2$ level in T_d symmetry.[18] The pentacoordinate complexes must also have lower symmetry than the pseudo-tetrahedral complexes, so the same number of transitions is expected. Furthermore, a crystal field calculation leads to the assignment of the band at *ca.* 20,000 cm^{-1} to an F → P transition and the band at *ca.* 12,000 cm^{-1} to the highest F→F transition.[19] This correspondence in assignments indicates that the crystal field splitting due to the donor atom set ON$_2$X$_2$ is fairly similar to that of the set N$_2$X$_2$. This can be partly ascribed to the weakness of the link with the ethereal oxygen atom.[20]

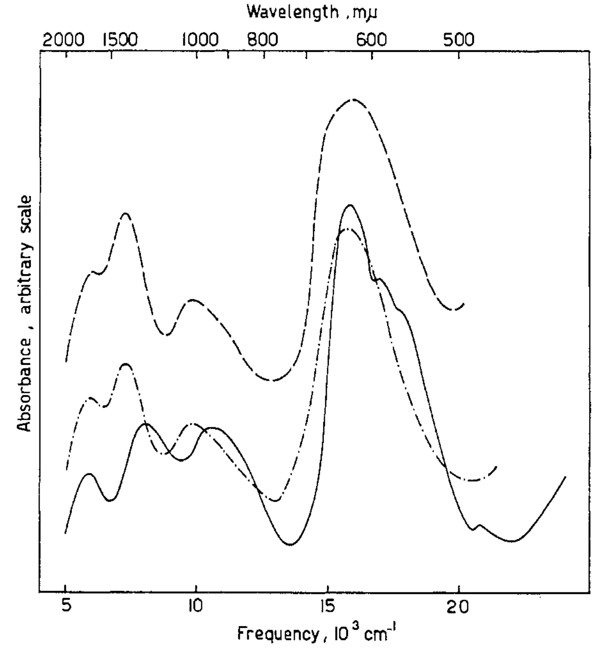

Figure 5.—Reflectance spectra of: Co(MOBtnNMe$_2$)Br$_2$, ———; Co(MOBenNEt$_2$)Br$_2$, - · - · - ·; Co((CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$)Br$_2$, — — —.

Cobalt(II) Complexes.—These complexes are blue and not very sensitive to moisture. They dissolve in polar organic solvents to give spectra which are practically identical with those obtained on the solid compounds. There are three maxima between 7000 and 10,000 cm^{-1} attributable to transitions between states derived from the ^4F free-ion term and a band with several subsidiary maxima around 18,000 cm^{-1} due to the F → P transition.[18b,21] These frequencies as well as the shape of the spectra are typical of distorted tetrahedral complexes (Figure 5), as particularly exemplified by Co((CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$)X$_2$,[11] which have the same donor atom set and presumably similar bond lengths and angles. The magnetic moments of 4.50–4.65 BM are usual for this type of structure.[22]

Thus the ligand MOBenNEt$_2$ (I, Y = O) behaves

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[17] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959); C. Furlani and G. Morpurgo, *Z. Physik. Chem.* (Frankfurt), **28**, 93 (1961).

[18] (a) C. Furlani and V. Valenti, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat., Nat.*, **32**, 942 (1962); (b) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, **4**, 139 (1965).

[19] M. Ciampolini, *ibid.*, **5**, 35 (1967); M. Ciampolini and I. Bertini, submitted for publication.

[20] The Ni–O bond length in the compound of ref 15 is 2.32 Å.

[21] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

[22] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

in the same way as MSBenNEt$_2$ (I, Y = S) in its interaction with cobalt(II) halides in giving only tetrahedral complexes, whereas MABenNEt$_2$ (I, Y = NH) gives only pentacoordinate complexes. This must reflect on the donor strength of oxygen and sulfur as compared with nitrogen, since to all intents and purposes the steric factors in the three ligands are identical.

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Absorption Spectral and Circular Dichroic Studies of Complexes of Hydroxy Acids with Praeseodymium Ion[1]

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Complexes of three types were characterized, according to the general pH range in which they were obtained, as acid, neutral, and alkaline complexes. All three could be obtained with many of the ligands. Spectra obtained could be attributed to effects of splitting both ground and excited states of the central metal ion. Each spectral transition apparently exhibited circular dichroism, so that a transition could be identified by either an absorption or dichroism component, as convenient. In the 430–510-mμ wavelength band, in which Pr(III) normally shows only three peaks of the $^3P_{2,1,0}$ multiplet and also has a buried $^1I_6$ transition, as many as 21 transitions could be recognized for the 1:1 alkaline tartrate complex. Correlation of the various spectra led to the following conclusions of chemical interest: acid complexes showed a sign of the CD defined by hydroxyl configuration at the α carbon; neutral complexes showed a sign of CD correlated with the sign of the lactone rotation which in turn is correlated with the sign of the hydroxyl configuration at the γ carbon, where this is an asymmetric center. Further conclusion was that seven-membered rings would form where the internal levels of the ligand favored this, six-membered rings would also form readily where this was the available choice, and under certain conditions, five-membered rings could form. Ligand acids used were tartaric, lactic, erythronic, ribonic, arabonic, xylonic, gluconic, gulonic, mannonic, idonic, galactonic, glucoheptonic, saccharinic, pantoic, malic, and saccharic acids.

Introduction

It has been shown[2] that rare earths form stable complexes with tartrate, with marked effects on the absorption spectra of the rare earth ions. Gray[3] has reported observing Cotton effects in the optical rotatory dispersion of alkaline tartrate solutions containing Nd(III), in the region of the Nd(III) absorption bands. Similar data have been obtained in this laboratory[4] for the Pr(III) complex, but it was obvious that the ORD technique was not suited to the fine-scale studies which the spectral alterations[2] made evident were needed.

The recent availability of a sensitive circular dichroism (CD) instrument has made it practical to reinvestigate the properties of rare earth complexes with optically active ligands and to map the correlations of the absorption and CD spectra. This paper will report the results of such a study with tartaric acid and a series of other hydroxy carboxylic acids as the ligands. Results with amino acids as the ligands will be reported separately.[5]

In addition to information on the spectral correlations mentioned, it has been possible to obtain considerable valuable information on chemical relations in the complex formation. Preliminary observations in this laboratory on the complexes of Nd(III), Er(III), etc., indicated fine-scale CD effects (*e.g.*, the 350-mμ band of neodymium(III) tartrate complex) which showed much more structure than was overt in the absorption spectrum. Investigations to be reported here are restricted to complexes of Pr(III), as the spectrum of this rare earth ion is simple enough to allow alterations to be followed in considerable detail.

Experimental Section

Spectral measurements were made with the Durrum–Jasco spectropolarimeter ORD-UV-CD-5. With Pr(III) concentrations of approximately 0.1 *M*, it was generally convenient to use 50-mm cells for the CD measurements, and 10-mm cells for the absorption spectra.

Most of the organic acids used in the study were available in the form of lactones, whose hydrolysis in water was quite variable with time and pH. The following procedure was therefore generally adopted. An amount of solid lactone sufficient almost to saturate 2 ml of water was dissolved to about that volume, and 2 or 3 drops of 5 *M* NaOH were added. When the pH of the mixture had settled back to pH 4 or less, indicating that anions had been formed, 1 ml of 0.3 *M* praeseodymium chloride solution (slightly acid) was added. Further additions of NaOH, as desired, increased the concentration of acid anion by further hydrolysis of lactone and ionization of the hydrolyzed acid.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).

[3] F. Gray, *Phys. Rev.*, **7**, 472 (1916).

[4] L. I. Katzin and R. W. Anderson, unpublished work.

[5] L. I. Katzin and E. Gulyas, in preparation.