TABLE I
POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	Pnma y	z	B, Å²
K	0.1776 (5)	0.25	0.1623 (6)	2.27 (8)
Br	0.07019 (18)	0.25	0.6847 (2)	1.59 (4)
O (1)	0.207 (2)	0.25	0.548 (2)	3.1 (3)
O (2)	0.914 (2)	0.25	0.577 (2)	3.7 (3)
O (3)	0.0811 (10)	0.0277 (17)	0.809 (1)	3.2 (2)

[a] Numbers in parentheses are standard deviations in the last figure(s).

I–O distances in the periodate ion.[7-9] The oxygen–oxygen distances within the configuration are: O(2)–(2)O(3) = 2.65 (2) Å, O(1)–(2)O(3) = 2.61 (2) Å, O(1)–O(2) = 2.63 (2) Å, and O(3)–O(3) = 2.63 (2) Å. The corresponding bond angles are: O(1)BrO(3) = 108° 48′, O(2)BrO(3) = 110° 12′, O(1)BrO(2) = 110° 11′, and O(3)BrO(3) = 108° 50′. Eight K–O distances are observed with contacts less than 3.08 Å as shown in Table III. The average weighted K–O distance is 2.92

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS

Å, corresponding essentially to the ionic radii sum corrected for the eightfold coordination.[10]

(7) M. R. Truter, D. W. J. Cruickshank, and G. A. Jeffery, *Acta Cryst.*, **13**, 855 (1960).

(8) H. G. Smith and H. A. Levy, *ibid.*, **15**, 1201 (1962).

(9) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp 334, 335.

(10) G. T. Seaborg and J. J. Katz, "The Actinide Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1954, p 775.

Results

KBrO₄ belongs to the BaSO₄ structure type and is therefore isostructural with several perchlorates reported in the literature.[6] Bond distances for KBrO₄ were computed with the Busing–Martin–Levy "Fortran Crystallographic Function and Error Program" and are shown in Table III.

TABLE III[a]
BOND DISTANCES (Å)

Br–O(1)	1.593 (14)	O(3)–O(3)	2.63 (2)
Br–O(2)	1.614 (16)	K–O(2′)	2.77 (2)
Br–(2)O(3)	1.617 (10)	K–(2)O(3‴)	2.93 (1)
O(2)–(2)O(3)	2.65 (2)	K–O(1)	2.90 (2)
O(1)–(2)O(3)	2.61 (2)	K–(2)O(3)	3.08 (1)
O(1)–O(2)	2.63 (2)	K–(2)O(3″)	2.84 (1)

[a] Numbers in parentheses are standard deviations in the last figure(s).

The BrO₄⁻ configuration is tetrahedral with Br–O(1) = 1.593 (14) Å, Br–O(2) = 1.614 (16) Å, and Br–(2)O(3) = 1.617(10) Å. Within error, the bond distances are equal, leading to an average value of 1.610 Å. This may be compared with values of 1.44–1.46 Å for Cl–O distances in the perchlorate ion and 1.79 Å for

(6) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, Interscience Publishers, New York, N. Y., 1965, p 45.

Coordination Chemistry of Phosphoryl Compounds. III. Transition Metal Complexes of Trimorpholinophosphine Oxide[1]

By J. T. DONOGHUE, E. FERNANDEZ,[2] AND
D. A. PETERS[3]

In a set of earlier papers, the coordination chemistry of hexamethylphosphoramide, [(CH₃)₂N]₃PO, was reported.[4-6] This ligand, found to be an oxygen donor in

(1) Part II: *J. Inorg. Nucl. Chem.*, in press.

(2) NSF Summer Undergraduate Research Participant.

(3) Undergraduate Research Participant.

(4) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(5) J. T. Donoghue and R. S. Drago, *ibid.*, **2**, 572 (1963).

(6) J. T. Donoghue and R. S. Drago, *ibid.*, **2**, 1158 (1963).

all cases investigated, exhibited a marked preference for tetrahedral geometry in complexes of the type [M-(HMPA)$_4$](ClO$_4$)$_2$ and in M(HMPA)$_2$X$_2$, where M = Co, Ni, Fe, Cu, or Mn and X = Cl, Br, or I. The complex Ni(HMPA)$_4$$^{2+}$ is the only known example of tetrahedral cationic Ni(II).[4] In investigating reasons for the peculiar preference of HMPA for tetrahedral geometry in such complexes, we have been studying complexes of ligands formally similar to HMPA in terms of basicity of the phosphoryl oxygen atom, but differing in terms of steric requirements. In this connection it was of interest to examine the complexes of (morph)$_3$PO (morph = morpholine)

$$\left(\underset{CH_2CH_2}{\overset{CH_2CH_2}{O \diagdown \diagup N}} \right)_3 PO$$
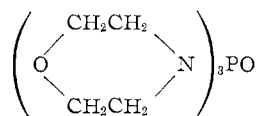
whose steric requirements should be similar to those of triphenylphosphine oxide, another ligand which is frequently found in tetrahedral complexes.

Experimental Section

Preparation of Compounds. CoX$_2$L$_2$ (X = Cl, Br, I, NCS).— Anhydrous halide (0.001 mol) was dissolved in 15 ml of hot absolute ethanol. To this solution was added 0.002 mol of ligand in 15 ml of hot absolute ethanol. The solution was stirred until cool, after which 75 ml of low-boiling (30–60°) petroleum ether was added to precipitate the solid compounds. The precipitates were washed under nitrogen five times with 10-ml portions of petroleum ether and filtered and dried under nitrogen. The dried solids were stored *in vacuo* over H$_2$SO$_4$.

NiX$_2$L$_2$ (X = Cl, Br, I, NCS, NO$_3$) and Co(NO$_3$)$_2$L$_2$.—The hydrated salts (0.001 mol) were treated with 15 ml of 2,2-dimethoxypropane as described earlier[4] to achieve dehydration. To this stirring solution, 15 ml of hot absolute ethanol containing 0.002 mol of ligand was added. Precipitation and filtration were accomplished in the same manner as for the cobalt compounds.

Analytical data for trimorpholinophosphine oxide and its complexes are presented in Table I.

spectrophotometer. The phosphoryl stretching frequencies of the free ligand and its complexes are reported in Table III.

Electronic spectral data for the complexes in the visible and near-infrared regions were obtained using a Cary Model 14 recording spectrophotometer. Some of the nickel complexes apparently decomposed in nitromethane and other solvents in which they were soluble. Data for these complexes are not reported. The yellow form of NiCl$_2$L$_2$ and the red form of NiI$_2$L$_2$ gave blue solutions in nitromethane and the spectra of these solutions were identical with those of the corresponding blue compounds.

Electronic spectral data for the remaining complexes are reported in Tables IV and V.

Magnetic Data.—Room-temperature magnetic susceptibilities of the solid complexes were measured by the Guoy method using an Alpha electromagnet. Guoy tubes were calibrated using solid Hg[Co(NCS)$_4$] as standard as described by Figgis and Nyholm.[7,8] Magnetic moments reported in Table VI are room-temperature (30°) values corrected for diamagnetic contributions, but not for temperature-independent paramagnetism.

Discussion

Significant reductions in the phosphoryl stretching frequency of the ligand in all complexes studied support the conclusion that trimorpholinophosphine oxide is coordinated *via* its phosphoryl oxygen in all complexes studied. The infrared spectra indicated the absence of water in the complexes. Conductivities of the complexes in nitromethane solutions are far lower than reported for typical electrolytes,[9] so it must be concluded that all complexes studied are essentially neutral, nonelectrolytic species in this solvent. From the analytical, infrared, and conductivity data, we conclude that the complexes contain trimorpholinophosphine oxide coordinated *via* its phosphoryl oxygen and may be formulated as nonlectrolytic, four-coordinate species of the type MX$_2$L$_2$ (except for X = NO$_3$).

The electronic spectra of the cobalt derivatives (Table IV) show the characteristic absorption band (ν_3) which is normally found for tetrahedral Co(II) derivatives. In addition, they show multicomponent bands (ν_2) in

Table I
Analytical Data[a]

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
L[b]	47.2	47.5	8.0	7.9	13.8	13.9
CoCl$_2$L$_2$	38.9	38.9	6.6	6.8	11.4	11.2
CoBr$_2$L$_2$	34.8	34.5	5.9	6.1	10.1	10.5
CoI$_2$L$_2$	31.2	30.9	5.3	5.7	9.1	9.0
Co(NCS)$_2$L$_2$	39.8	39.8	6.2	6.0	14.3	14.0
Co(NO$_3$)$_2$L$_2$	36.3	36.1	6.1	6.1	14.1	14.1
NiCl$_2$L$_2$ (blue)	38.9	38.6	6.6	6.6	11.4	11.2
NiCl$_2$L$_2$ (yellow)	38.9	38.4	6.6	6.4	11.4	11.2
NiBr$_2$L$_2$	34.8	34.7	5.9	5.9	10.1	9.6
NiI$_2$L$_2$ (blue)	31.2	31.5	5.3	5.5	9.1	9.2
NiI$_2$L$_2$ (red)	31.2	31.0	5.3	5.3	9.1	9.3
Ni(NCS)$_2$L$_2$	39.8	39.5	6.2	6.1	14.3	14.0
Ni(NO$_3$)$_2$L$_2$	36.3	36.2	6.1	6.6	14.1	14.0

[a] Analyses by A. Bernhardt, West Germany. [b] L designates trimorpholinophosphine oxide.

Conductance Measurements.—Measurements of conductivities of 0.001 *M* solutions of the complexes in nitromethane are reported in Table II. The results were obtained using an Industrial Instruments bridge and cell which had been previously calibrated with 0.01 *N* KCl solutions.

Spectral Data.—Infrared spectra of mulls of the ligand and its complexes were obtained using a Perkin-Elmer 337 recording

the near-infrared region, also characteristic of tetrahedral Co(II).

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(8) B. M. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 403.

(9) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

TABLE II

CONDUCTIVITIES OF 0.001 M SOLUTIONS IN
NITROMETHANE AT 30°

Compound	Λ_M	Compound	Λ_M
$CoCl_2L_2$	2.3	$NiCl_2L_2$ (blue)	3.1
$CoBr_2L_2$	2.4	$NiBrL_2$	2.0
CoI_2L_2	2.1	NiI_2L_2 (blue)	3.1
$Co(NCS)_2L_2$	2.7	NiI_2L_2 (red)	4.5
$Co(NO_3)_2L_2$	2.1	$Ni(NCS)_2L_2$	2.5
$NiCl_2L_2$ (yellow)	2.3	$Ni(NO_3)_2L_2$	4.0

TABLE III

INFRARED PHOSPHORYL FREQUENCIES OF NUJOL MULLS

Compound	ν_{P-O}, cm^{-1}	Compound	ν_{P-O}, cm^{-1}
L	1203	$NiCl_2L_2$ (blue)	1160
$CoCl_2L_2$	1160	$NiBr_2L_2$	1155
$CoBr_2L_2$	1158	NiI_2L_2 (blue)	1156
CoI_2L_2	1151	NiI_2L_2 (red)	1160
$Co(NCS)_2L_2$	1160	$Ni(NCS)_2L_2$	1160
$Co(NO_3)_2L_2$	1152	$Ni(NO_3)_2L_2$	1190
$NiCl_2L_2$ (yellow)	1157		

TABLE IV

ELECTRONIC SPECTRAL DATA FOR CoX_2L_2–0.001 M
CH_3NO_2 SOLUTIONS

Complex	ν_3, λ_{max}, mμ	ν_2, λ_{max}, mμ
$CoCl_2L_2$	580 ($\sim$700)[a]	1350 ($\sim$40)[a]
	648 ($\sim$700)	1600 ($\sim$40)
	672 ($\sim$700)	1750 ($\sim$42)
$CoBr_2L_2$	620 (385)	1375
	648 (415)	1600 ($\sim$45)
	710 (445)	1900
CoI_2L_2	620 (410)	1450
	655 (515)	1650 ($\sim$70)
	720 (480)	1850
$Co(NCS)_2L_2$	605	1325
	620 ($\sim$775)	1510
	630	
$Co(NO_3)_2L_2$	550 (130)	1250 (10)

[a] Designates molar extinction coefficient ϵ_{max} at λ_{max}.

TABLE V

ELECTRONIC SPECTRAL DATA FOR NiX_2L_2–0.001 M
CH_3NO_2 SOLUTIONS

Compound	ν_3, λ_{max}, mμ	ν_2, λ_{max}, mμ
$NiCl_2L_2$ (blue)	560 ($\sim$100)	1120 (15)
	581	1400 sh
		1550 sh
$NiBr_2L_2$	600 (150)	1210 (15)
		1290 sh
		1600 sh
NiI_2L_2	575 ($\sim$200)	1150 (30)
$Ni(NO_3)_2L_2$	450 (30)	
	700 (10)	
	750 (10)	
	760 sh	
$Ni(NCS)_2L_2$		

TABLE VI

ROOM-TEMPERATURE (30°) MAGNETIC MOMENTS
OF THE COMPLEXES

Compound	$10^6\chi_M$	$10^6 \times$ diamag contrib, cgs units	$10^6\chi'_M$	μ_{eff}, BM
$CoCl_2L_2$	8508	417	8925	4.67
$CoBr_2L_2$	9167	438	9605	4.85
CoI_2L_2	9456	466	9922	4.91
$Co(NCS)_2L_2$	8227	438	8665	4.61
$Co(NO_3)_2L_2$	7666	414	8080	4.45
$NiCl_2L_2$ (yellow)[a]				
$NiCl_2L_2$ (blue)	6083	417	6500	3.99
$NiBr_2L_2$	6012	438	6450	3.97
NiI_2L_2 (red)[a]				
NiI_2L_2 (blue)	5944	466	6405	3.95
$Ni(NCS)_2L_2$[a]				
$Ni(NO_3)_2L_2$	4336	414	4750	3.41

[a] Diagmagnetic.

in that the spectral and magnetic results are somewhat ambiguous. Absorption intensities are rather lower than for the halo derivatives but significantly higher than for typical octahedral cobalt(II). The magnetic moment (Table VI) would tend to indicate a tetrahedral environment, but earlier work with nitrato ligands[12] prompts us to assume the presence of bidentate nitrate and therefore that this complex is an example of six-coordinate cobalt(II).

The results are similar for nickel(II) complexes of (morph)$_3$PO. From the analytical (Table I), conductivity (Table II), and infrared (Table III) data, we conclude that these species may be formulated as non-electrolytic, four-coordinate (except for X = NO$_3$), oxygen-coordinated derivatives of the type [NiX$_2$L$_2\cdot$]. The electronic spectra of these species (Table V) exhibit long-wavelength absorption and absorption intensities very much higher than would be expected for Ni(II) in centrosymmetric fields.[9] The over-all features of the spectral and magnetic properties are once again in accord with a ligand field about Ni(II) which is primarily cubic[13–17] upon which a lower symmetry C$_{2v}$ component is superposed. The same effects of intensity variation with concentration as were noted for Co(II) complexes were also exhibited by the Ni(II) complexes.

It is concluded that the complexes M(NO$_3$)$_2$L$_2$ (M = Ni, Co) probably contain bidentate nitrato ligands, a conclusion which has been reached by others in similar work.[18–22]

The compound Ni(NCS)$_2\cdot$2(morph)$_3$PO is diamagnetic and does not exhibit spectral properties similar to those of octahedral or tetrahedral nickel(II). It is as-

The spectral and magnetic data may be interpreted in terms of a predominantly hemihedric cubic field about cobalt(II) upon which is superposed a contribution from a lower symmetry C$_{2v}$ component.[10,11]

The nitrate complex presents an interesting situation

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(19) F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.*, 84, 2013 (1962).

(20) J. G. Bergman and F. A. Cotton, *ibid.*, 86, 2941 (1964).

(21) C. Furlani, *Gazz. Chim. Ital.*, 88, 279 (1958).

(22) C. Furlani and G. Sartori, *J. Inorg. Nucl. Chem.*, 8, 127 (1958).

sumed that the complex is an example of nickel(II) in a planar environment.

On the basis of evidence presented in earlier sections, it is concluded that the compounds CoX_2L_2 (X = Cl, Br, I, NCS) contain Co(II) in pseudotetrahedral environments and the compounds NiX_2L_2 (X = Cl, Br, I) for which two solid forms can be isolated (diamagnetic and paramagnetic) contain planar and tetrahedral Ni(II), respectively. Both solid modifications dissolve in CH_3-NO_2 to give solutions containing predominantly tetrahedral nickel. Interconversion of modifications can be achieved easily. The planar isomers may be converted to tetrahedral by dissolution in a suitable solvent or in the solid phase by heating at 110°. The tetrahedral forms revert to planar upon standing for several weeks. The compound $Ni(NCS)_2 \cdot 2(morph)_3PO$ has been assigned a planar structure while it was not possible to make a definite assignment for $M(NO_3)_2 \cdot 2HMPA$ (M = Co(II), Ni(II)).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Tridentate Schiff Base Complexes of Copper(II)[1,2]

BY WILLIAM E. HATFIELD AND FRED L. BUNGER

Tridentate Schiff base ligands yield complexes with copper(II) which frequently exhibit unusual properties. The low magnetic moment observed by Kishita, Muto, and Kubo[3] for acetylacetonemono(*o*-hydroxyanil)copper(II) stimulated extensive structural and magnetic investigations,[4-7] and these have led to a better understanding of the mechanisms of spin–spin coupling in magnetically condensed complexes. Unusual structures have also been obtained with these ligand systems. For example, pyridine-2-carboxaldoxime forms a trinuclear copper complex with a tridentate sulfate ion and four-coordinated oxygen.[8] In order to identify some of the factors which contribute to the donor prop-

erties of tridentate ligands, we have prepared and characterized a series of complexes with these ligands in which the donor atoms, the substituents on the donor atoms, and the donor atom linkages have been systematically varied. Here we report the results of our work with ligands having two nitrogen and one oxygen donor atoms.

Experimental Section

Preparation of the Complexes. N-(2-Dimethylaminoethyl)-salicylaldiminatocopper(II) Nitrate.—A series of complexes were prepared with substituted salicylaldehydes and N,N-dimethylethylenediamine. The appropriate salicylaldehyde (10 mmol) and N,N-dimethylethylenediamine (0.88 g, 10 mmol) were dissolved in 200 ml of isopropyl alcohol, and the resultant solution was heated at reflux for approximately 20 min. Copper nitrate trihydrate (1.20 g, 5 mmol) in 50 ml of anhydrous methyl alcohol and solid basic copper carbonate (0.55 g, 2.5 mmol) were added to the boiling solution, and the mixture was stirred vigorously while maintained at reflux for 30 min. The solution was filtered and reduced by evaporation to a volume of 150 ml. The dark green crystals which separated were collected on a Büchner funnel and washed with two 20-ml portions of isopropyl alcohol. The analytical data are given in Table I.

Schiff Bases Containing a Pyridine Ring.—Compounds VI–IX shown below in the most simple but not necessarily struc-

VI

VII

VIII

IX
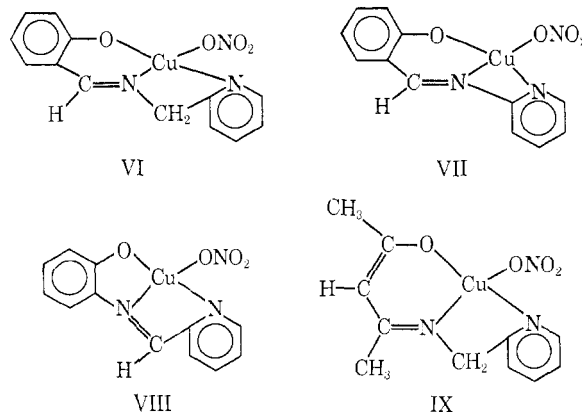
turally correct formulations were prepared by the same general procedure described above. Ethyl alcohol was used as the solvent. The analytical data are given in Table II.

Physical Measurements.—Magnetic susceptibilities were determined at room temperature and at 77°K using procedures described previously.[9] Infrared spectra of mulls and chloroform solutions were recorded on a Perkin-Elmer Model 137 spectrophotometer, visible spectra with a Cary Model 14 spectrophotometer, and conductivities of nitrobenzene solutions with a standard bridge. The experimental details and supporting data will be tabulated elsewhere.[10]

Results and Discussion

The most interesting result of this work obtains with compound VII. The infrared spectrum shows bands at 1020, 1310, and 1520 cm^{-1} which are due to coordinated nitrate,[11] and the conductivity of 3.12 ohm^{-1} in a 10^{-3} M nitrobenzene solution[12] confirms the infrared results. The magnetic moment at room temperature is 1.3 BM per copper ion, and this decreases to 1.0 BM

(1) This is part X of the series "Spin–Spin Coupling in Magnetically Condensed Complexes."

(2) This research was supported by the National Science Foundation.

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(12) See, for example, F. Morris and R. S. Nyholm, *ibid.*, 4375 (1956).