Results and Discussion

The magnetic susceptibility or $Tl_2[Re(SCN)_6]$, Table I, is essentially the same as that reported by Nelson and Boyd.[2] That for $Cs_2[Re(SCN)_6]$ is also in the expected range, almost the same as reported for the potassium salt. It thus appears that these authors did, in fact, have authentic material.

The ultraviolet–visible spectra (Table II, Figures 1 and 2) show two intense charge-transfer bands and a series of low-intensity peaks which appear to be the ligand field transitions. These are superimposed on the tail of the 23,800-cm^{-1} band, and the extinction coefficients given in Table II were obtained by subtracting this background. There is a distinct similarity between the more intense bands of this region and those observed[5] for other octahedral Re(IV) complexes such as $[ReCl_6]^{2-}$. This latter spectra has been assigned.[6] However, a number of other peaks, all of low intensity, appear in the thiocyanate complex. The energies of this series of bands lie about 3000 cm^{-1} below those of the hexachloride.

TABLE III

INFRARED SPECTRA OF $[Re(SCN)_6]^{2-}$ COMPOUNDS (CM^{-1})

Compound	C≡N stretch	C—S stretch
KSCN	2049	749
$Cs_2[Re(SCN)_6]$	2040, 2022	699
$Tl_2[Re(SCN)_6]$	2038	694
$Ag_2[Re(SCN)_6]$	2038	695

The infrared spectra (Table III, Figure 3) show only the expected thiocyanate peaks. From the arguments of Tramer,[7] and Lewis *et al.*,[8] the decrease in the C–S stretching frequency to about 700 cm^{-1} in our products is indicative of sulfur bonding to the rhenium. The C–N frequency is unusually low, but no significance can be attributed to this at present. No trace of any Re=O can be seen in the spectra.

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(5) R. A. Bailey and J. A. McIntyre, *Inorg. Chem.*, **5**, 964 (1966).
(6) J. C. Eisenstein, *J. Chem. Phys.*, **34**, 1628 (1961).
(7) A. Tramer, *J. Chim. Phys.*, **59**, 232 (1962).
(8) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

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Amides as Ligands. VII. Complexes of N-Methyl-γ-butyrolactam with Nontransition Metals

BY STANLEY K. MADAN

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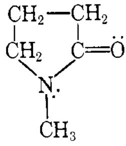
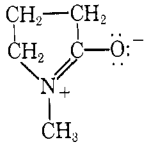
The first two papers of this series reported the formation and characterization of coordination compounds of several transition metals and a few nontransition metal ions with the ligands N,N-dimethylacetamide[1] and ε-caprolactam.[2,3] The present work is concerned with N-methyl-γ-butyrolactam (NMBuL) complexes of nontransition elements, especially alkali and alkaline earth elements. The structure of NMBuL is best represented by



I



II

Few stable complexes of alkali metals have been reported. Complexes of the alkali metals with β-diketone derivatives, *o*-nitrophenol, and salicylaldehyde have been described in the literature.[4,5] The sodium compounds ranged from hydrated ionic salts such as $Na(acac)\cdot 2H_2O$ to adducts such as Na(Sal)HSal (HSal = salicylaldehyde). Pfeiffer[6] and others[7] have reported the isolation of a complex of sodium perchlorate with 1,10-phenanthroline. Brady and Badger[8] have presented evidence for chelation in sodium salts of *o*-hydroxybenzaldehydes. More recently, Popp and Joesten[9] have isolated and characterized a number of alkali metal and alkaline earth metal salts with the ligand octamethylpyrophosphoramide (OMPA). Gentile and co-workers[10] have also reported complexes of diacetamide with alkali and alkaline earth metal salts.

In line with our interest in substituted amides as ligands, we decided to extend our studies of NMBuL by studying reactions of NMBuL with nontransition metal ions. During the progress of this study a paper appeared in which a few NMBuL–transition metal complexes were described and characterized *via* their infrared spectra, magnetic moments, and electrical conductivity.[11]

Experimental Section

Reagents.—We are thankful to General Aniline and Film Corp. for furnishing us with a sample of NMBuL. This product was distilled under reduced pressure. The constant-boiling middle fraction, 80° (10 mm), $n^{25}D$ 1.4691, was collected. This refractive index is in agreement with the one reported in the literature.[12] Metal perchlorates were purchased from G. Frederick Smith Chemical Co.

Preparation of Complexes.—All of the NMBuL complexes with metal perchlorates with the exception of that of Mg(II) were prepared by the same procedure. The hydrated metal perchlorates were dehydrated with excess quantities of 2,2-dimethoxypropane by stirring (magnetic) for a minimum of 2 hr. Excess NMBuL was added and stirring continued for 40–50 min. Excess anhydrous ether was added, and crystalline product formed

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(1) W. E. Bull, S. K. Madan, and J. Willis, *Inorg. Chem.*, **2**, 303 (1963).
(2) S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965).
(3) J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *Inorg. Chem.*, **4**, 18 (1965).
(4) N. W. Sidgewick and F. M. Brewer, *J. Chem. Soc.*, **127**, 2379 (1925).
(5) F. M. Brewer, *ibid.*, 361 (1931).
(6) P. Pfeiffer and W. Christeleit, *Z. Anorg. Allgem. Chem.*, **239**, 133 (1938).
(7) A. A. Schilt and R. O. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).
(8) O. L. Brady and W. H. Badger, *J. Chem. Soc.*, 952 (1932).
(9) C. J. Popp and M. D. Joesten, *Inorg. Chem.*, **4**, 1418 (1965).
(10) P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem.*, **27**, 2301 (1965).
(11) R. J. Niedzielski and G. Zinder, *Can. J. Chem.*, **43**, 2618 (1965).
(12) E. Fisher, *J. Chem. Soc.* 1382 (1955).

TABLE I

ANALYTICAL AND OTHER DATA FOR NMBuL COMPLEXES

Compound	% carbon		% hydrogen		% nitrogen						
	Theory	Found	Theory	Found	Theory	Found	% other	Theory	Found	Mp, °C	% yield
$Li(NMBuL)_4ClO_4\cdot 2H_2O$	44.60	44.23	7.43	6.93	10.38	9.80	ClO_4	18.40	19.00	42	76
$Na(NMBuL)_2ClO_4\cdot H_2O$	35.60	35.36	5.93	5.64	8.28	8.21	ClO_4	29.40	29.84	53–57	95
$Mg(NMBuL)_6(ClO_4)_2$	44.30	43.73	6.63	6.85	10.27	10.62	ClO_4	24.40	24.04	170	80
$Ca(NMBuL)_6(ClO_4)_2$	43.30	43.94	6.49	7.13	10.07	9.50	ClO_4	23.90	23.95	130	92
$Sr(NMBuL)_6(ClO_4)_2$	40.90	40.32	6.13	6.48	9.54	9.40	ClO_4	22.62	22.65	53–55	90
$Al(NMBuL)_6(ClO_4)_3$	39.20	39.99	5.87	6.39	9.13	9.40	ClO_4	32.30	31.48	221 dec	85
$Zn(NMBuL)_4(ClO_4)_2$	36.35	36.02	5.49	5.25	8.48	8.47	Zn	9.87	9.50	193 dec	82
$Cd(NMBuL)_6(ClO_4)_2$	39.90	39.77	5.95	5.88	9.32	8.74	Cd	13.95	14.00	140	89
$In(NMBuL)_6(ClO_4)_2$	35.80	36.04	5.37	4.88	8.35	8.47	ClO_4	29.70	29.60	190 dec	90
$Zn(NMBuL)_2(NO_3)_2$	31.20	31.30	4.67	5.20	14.54	13.98	Zn	16.80	16.84	93	60
$Cd(NMBuL)_3(NO_3)_2$	33.90	34.00	5.07	5.58	13.10	12.49	NO_3	21.10	20.39	82–84	65
$Mg(NMBuL)_3(NO_3)_2\cdot 2H_2O$	37.40	37.20	6.45	6.71	14.65	14.15	Mg	4.98	5.00	...	40
$Li(NMBuL)_2NO_3\cdot H_2O$	42.30	41.56	6.32	6.97	14.72	14.65	NO_3	21.70	21.20	64	60
$Ca(NMBuL)_2Cl_2\cdot 4H_2O$	31.60	32.10	6.84	5.71	7.37	7.08	Ca	10.60	11.38	170 dec	62
$Sb(NMBuL)_2Cl_3\cdot 4H_2O$	23.60	23.51	5.12	4.78	5.53	5.42	...	...	...	53	50
$Li(NMBuL)Cl$[a]	...	...	...	...	...	...	...	...	...	136	62

[a] This compound is reported in ref 10.

immediately for Al(III), In(III), Ca(II), Sr(II), Zn(II), and Cd(II). The mixtures were filtered, and the precipitates were washed six to seven times with ether and dried *in vacuo*. The lithium and sodium perchlorate complexes with NMBuL came down as viscous oily materials which could be worked up by successively evaporating the solvent and treating with ether. They were recrystallized from methanol with great difficulty. All of the metal perchlorate complexes with NMBuL are very stable, but the lithium and sodium complexes are very hygroscopic.

The magnesium perchlorate complex with NMBuL was synthesized by adding anhydrous magnesium perchlorate dissolved in a very small amount of methanol to NMBuL. This mixture was stirred for 30 min. A crystalline product was obtained immediately upon adding anhydrous ether. The NMBuL complexes of calcium and lithium chlorides were prepared by dissolving the anhydrous chlorides in a minimum amount of methanol, adding an excess of NMBuL, and stirring for 20 min. Anhydrous ether was added and the resulting oils were worked up. The procedure employed for hydrated metal perchlorates was extended to hydrated magnesium chloride. The resulting oil was worked up to give a white solid. This material was very poorly characterized. As shown in Table I, a completely anhydrous complex of NMBuL with metal chloride salts could not be isolated. Hydrated lithium, magnesium, calcium, zinc, and cadmium nitrates were dissolved in a minimum of methanol and stirred with an excess of NMBuL for 1–2 hr. Ether was added and the resulting oils were worked up with ether to form solids. The calcium NMBuL complex was very poorly characterized. Elemental analyses for all of the complexes synthesized in this work are shown in Table I.

Instrumentation.—Infrared spectra were obtained with Perkin-Elmer Model 137 and 521 recording spectrophotometers. The spectra were frequency calibrated using a polystyrene film. X-Ray diffraction patterns were obtained using a General Electric Model XRD-5 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.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England, and some metal ions, perchlorates, and nitrates were done in our laboratory. Perchlorate and nitrate were determined by using the nitron reagent.[13] Metal analyses were determined by EDTA titration.[14]

Results and Discussion

General.—All of the complexes reported in Table I are new. Spectral data are given in Table II. The reaction between NMBuL and most of the perchlorates of nontransition metals, carried out as described in the Experimental Section, yields well-crystallized products. On the basis of the analyses and infrared measurements they may be formulated as the perchlorates of hexakis-(N-methyl-γ-butyrolactam)metal cation, $[M(NMBuL)_6]^{n+}$ ($M = Ca^{2+}, Mg^{2+}, Sr^{2+}, Cd^{2+}, Al^{3+}$, and In^{3+}), and tetrakis(N-methyl-γ-butyrolactam)-metal cation, $[M(NMBuL)_4]^{n+}$ ($M = Li^+$ and Zn^{2+}).

TABLE II

INFRARED SPECTRA FOR NMBuL COMPLEXES (CM^{-1})

Compound	$\nu_{C=O}$	$\Delta\nu_{C=O}$	ν_{C-N}	$\Delta\nu_{C-N}$	ν_{ClO_4}
NMBuL	1690	...	1110	...	...
$Li(NMBuL)_4ClO_4\cdot 2H_2O$	1650	−40	Masked by ClO_4		1100
$Na(NMBuL)_2ClO_4\cdot H_2O$	1650	−40	Masked by ClO_4		1100
$Mg(NMBuL)_6(ClO_4)_2$	1650	−40	Masked by ClO_4		1098
$Ca(NMBuL)_6(ClO_4)_2$	1660	−30	Masked by ClO_4		1092
$Sr(NMBuL)_6(ClO_4)_2$	1660	−30	Masked by ClO_4		1092
$Al(NMBuL)_6(ClO_4)_3$	1630	−60	Masked by ClO_4		1092
$In(NMBuL)_6(ClO_4)_3$	1625	−65	Masked by ClO_4		1100
$Zn(NMBuL)_4(ClO_4)_2$	1625	−65	Masked by ClO_4		1100
$Cd(NMBuL)_6(ClO_4)_2$	1640	−50	Masked by ClO_4		1100
$Zn(NMBuL)_2(NO_3)_2$	1640	−50	1130	+20	...
$Cd(NMBuL)_3(NO_3)_2$	1640	−50	1120	+10	...
$Mg(NMBuL)_3(NO_3)_2\cdot 2H_2O$	1640	−50	1120	+10	...
$Li(NMBuL)_2NO_3\cdot H_2O$	1650	−40	1125	+15	...
$Li(NMBuL)Cl$[a]	1625	−65	1120	+10	...
$Ca(NMBuL)_2Cl_2\cdot 4H_2O$	1640	−50	1125	+15	...
$Sb(NMBuL)_2Cl_3\cdot 4H_2O$	1610	−80	1120	+10	...

[a] Reported in ref 10.

In the crystalline state the complex salts are remarkably stable in air. In aqueous solution they decompose immediately with separation of the hydrolysis products. The crystalline salts have a reasonable thermal stability. Most of them are unaltered up to 130°.

Infrared Spectra.—The structure of NMBuL is

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(13) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand and Co., Inc., New York, N. Y., 1947.

(14) H. A. Flaschka, "EDTA Titrations," Pergamon Press Inc., New York, N. Y., 1959.

TABLE III

INFRARED BANDS PERTINENT TO THE STATE OF NITRATE ION IN THE NMBuL–NITRATE COMPLEXES

Observed bands,[a] cm^{-1}					Accepted bands, cm^{-1} [25]		
$Zn(NMBuL)_2(NO_3)_2$	$Cd(NMBuL)_3(NO_3)_2$	$Li(NMBuL)_2NO_3 \cdot H_2O$	$Mg(NMBuL)_3(NO_3)_2 \cdot 2H_2O$	Assignment	$Ni(en)_2(NO_3)_2$ monodentate nitrate	$Ni(dien)(NO_3)_2$ monodentate and bidentate nitrate	$[Ni(tetb)NO_3]NO_2$ ionic and bidentate nitrate
840 m, sp	838 m, sp	827 m, sp	810 m, sp	ν_2	818 m, sp	816 m, sp	825 m, sp
815 m, sp	818 m, sp			(out-of-plane def)		808 m, sp	806 m, sp
	1330 s			ν_3		1315 s	
1370 s, br	1470 s			(doubly degenerate		1440 s	1375 s, br
1290 s	1300 s	1300 s	1305 s	str)	1307 s	1300 s	1280 s
1475 s	1490	1430 s	1420 s		1420 s	1480 s	1490 s
	725 w, br			ν_4		714 vw, sp	
720 vw	740 w, sp			(doubly degenerate		736 vw, sp	
680 vw	675 vw	675 w, sp	685 w, sp	in-plane	708 w, sp	698 vw, sp	695 vw
750 w, br	752 w, sp	722 w, br	725 w, br	bending)	728 w, sp	849 w, sp	745 w, sp

[a] s, strong; m, medium; w, weak; v, very; br, broad; sp, sharp.

best described as a resonance hybrid of primary structures I and II. Since this molecule has two possible centers for coordination, either through the oxygen or through the nitrogen, one of our first considerations in this research was the position of coordination. The infrared spectra of lactams have been studied by several workers.[15,16] Recently, Gentile, *et al.*,[10] have attributed the characteristic frequency at 1690 cm^{-1} to the C=O stretching frequency in the NMBuL molecule. By running the NMBuL neat between the sodium chloride windows, we observe the same stretching frequency (1690 cm^{-1}). The shift of the C=O stretch in all cases is in the direction of lower frequency (Table II). This is indicative of bond weakening and decrease in double-bond character of C=O with electron density being drawn away by interaction with the metal ion. The relative strength of the interaction is indicated by the magnitude of the shift.[17,18] This in itself is evidence for the use of carbonyl donor site. Further evidence for coordination through the carbonyl oxygen is found by examining the C—N stretching frequency, which shifts to higher frequencies in all cases and is shown in Table II. The decrease in the C=O bond order that occurs when the metal ion coordinates to the carbonyl oxygen can cause the lone pair on nitrogen to delocalize into the available p_π orbitals of the carbon. This would increase the C—N bond order.

The presence of water in $Mg(NMBuL)_3(NO_3)_2 \cdot 2H_2O$, $Ca(NMBuL)_2Cl_2 \cdot 4H_2O$, $Na(NMBuL)_2ClO_4 \cdot H_2O$, $Li(NMBuL)_4ClO_4 \cdot 2H_2O$, $Li(NMBuL)_2NO_3 \cdot H_2O$, and $SbCl_3(NMBuL)_2 \cdot 4H_2O$ was established by an absorption peak in the 3300–3400-cm^{-1} region of the infrared spectrum[19] of each of these compounds. This peak is absent in all of the other complexes.

The infrared spectra of $Zn(NMBuL)_2(NO_3)_2$, $Cd(NMBuL)_3(NO_3)_2$, $Mg(NMBuL)_3(NO_3)_2 \cdot 2H_2O$, and $Li(NMBuL)_2NO_3 \cdot H_2O$ were investigated to obtain evidence for ionic or coordinated nitrate ions. The infrared spectrum of coordinated nitrate ion has previously been described.[20–24] More recently, Curtis[25] has reported that the nitrate ion in ionic compounds exhibits three bands: ν_2 (out-of-plane deformation), ν_3 (doubly degenerate stretch), and ν_4 (doubly degenerate in-plane bending). When the nitrate ion is coordinated as a monodentate or bidentate ligand, all bands become active, shifts in band positions and intensities are observed, and the degeneracy of ν_3 and ν_4 is lifted. For a coordinated monodentate nitrate ion, ν_3 is weakened and there is splitting of ν_3 and ν_4, and a small shift of ν_2 to lower frequency. However, for both a coordinated bidentate and a monodentate nitrate ion, an enhancement and further splitting of the above modes is observed. The ν_3 and ν_4 split into four bands while the ν_2 split into two bands. Table III shows a comparison of the infrared spectra of the NMBuL–nitrate complexes, along with some model compounds in which a monodentate, monodentate and bidentate, or ionic and bidentate nitrate ions are present.[25]

The infrared spectrum of $Zn(NMBuL)_2(NO_3)_2$ provides evidence that this complex contains both an ionic and a bidentate nitrate ion. The spectrum of $Cd(NMBuL)_3(NO_3)_2$ seems to indicate the presence of a monodentate nitrate ion and also a bidentate one, whereas the infrared spectra of $Mg(NMBuL)_3(NO_3)_2 \cdot 2H_2O$ and $Li(NMBuL)_2(NO_3) \cdot H_2O$ point to the fact that both these compounds contain monodentate nitrate ions.

X-Ray Powder Diffraction.—The positions and relative intensities of d_{hkl} for the 6:1 complexes are given in Table IV. The d_{hkl} values of $Ni(NMBuL)_6(ClO_4)_2$ are included for comparison. The X-ray data indicate that the 6:1 complexes are isomorphous. Earlier work with the spectra of $Ni(NMBuL)_6(ClO_4)_2$ dissolved

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(15) W. Klemperer, M. W. Cronym, A. H. Maki, and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 5846 (1954).

(16) R. Mecke, Jr., and R. Mecke, Sr., *Chem. Ber.*, **89**, 343 (1956).

(17) K. Nakamoto, F. Junnosuice, and S. Tanaka, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

(18) R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958).

(19) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(20) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

(21) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957); *J. Inorg. Nucl. Chem.*, **8**, 75 (1958).

(22) C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960); B. M. Gatehouse and A. E. Comyns *ibid.*, 3965 (1958).

(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963; E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

(24) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959).

(25) N. F. Curtis and Y. M Curtis. *Inorg. Chem.*, **4**, 804 (1965).

TABLE IV

X-RAY POWDER PATTERN DATA

$Mg(NMBuL)_6(ClO_4)_2$		$Ca(NMBuL)_6(ClO_4)_2$		$Sr(NMBuL)_6(ClO_4)_2$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}
10.52	18	11.04	4	10.77	29
6.10	20	6.32	14	6.27	56
5.30	42	5.47	9	5.21	12
4.79	15	4.92	26	4.87	44
4.37	100	4.48	63	4.43	9
3.72	28	3.93	4	3.76	24
3.53	18	3.78	9	3.63	50
3.26	15	3.63	14	3.37	6
3.11	8	3.14	5	3.29	5
2.74	8	2.88	2	2.81	15
2.31	8	2.83	4	2.32	13
$Cd(NMBuL)_6(ClO_4)_2$		$In(NMBuL)_6(ClO_4)_3$		$Ni(NMBuL)_6(ClO_4)_2$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{kkl}	I/I_{100}
10.91	75	10.27	75	11.18	100
6.27	47	6.50	11	6.96	10
5.43	4	5.30	5	5.63	10
4.87	50	4.69	13	4.97	40
4.43	95	4.15	64	4.76	100
3.62	35	4.00	45	4.31	50
3.27	23	3.91	13	4.05	30
2.90	5	2.90	5	3.00	10
2.71	18	2.84	5	2.85	5
2.37	17	...	..	2.50	8

in nitromethane and NMBuL supported the assignment of an octahedral configuration to this complex in solution.[3] The similarity of X-ray data for the 6:1 complexes in this study supports the assignment of an octahedral configuration to the metal ions in these complexes.

Acknowledgment.—The author is indebted to the Research Foundation of the State University of New York for Grant-in-aid No. F-64-40-1 for partial support of this project and for summer fellowships for 1965 and 1966. The author also wishes to thank Miss Linda Herman for her assistance in some phases of this work.

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Phthalocyaninato(2—)chromium(III) Phosphinates

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Among the chromium(III) derivatives of phthalocyanine described by Elvidge and Lever[2] is $CrPcOOCCH_3$[3] to which they originally assigned a polymeric structure. This structure (recently withdrawn by one of the authors[4]), the evidence Kenney and his coworkers have collected for the polymeric nature of several phthalocyanine derivatives of group IVb elements,[5] and our work on the polymeric nature of metal phosphinates[6] suggested that it would be of interest to examine phthalocyaninato(2−)chromium(III) phosphinates.

Experimental Section

Reagents.—$Cr(CO)_6$ was obtained from Diamond Alkali Co., and the phthalonitrile, from Eastman Organic Chemicals Co. The latter was recrystallized from benzene prior to use. The phosphinic acids were prepared in our laboratories by methods previously described.[7] Other reagents and solvents used were the best grades commercially available.

CrPc.—About 1 g of $Cr(CO)_6$, weighed exactly by difference, was placed in a continuous-infusion extractor[8] containing a fritted-glass disk and equipped with a stopcock in the drain. With the stopcock closed, 20 ml of benzene was added, and then the condenser was attached. A slight excess of phthalonitrile and 150 ml of 1-chloronaphthalene were added to the pot, the apparatus was purged thoroughly with nitrogen, and the phthalonitrile solution was brought to reflux (225°) with stirring while a slow stream of nitrogen passed through the apparatus. After reflux started, the stopcock were opened slightly to permit the benzene solution to drop into the refluxing 1-chloronaphthalene at such a rate that the temperature remained between 230 and 252°. Under these conditions the benzene flashed out of the pot, was condensed, and dissolved more $Cr(CO)_6$. Refluxing was continued about 30 min beyond the time required to dissolve all of the $Cr(CO)_6$ (total time 3–5 hr). After the reaction mixture cooled to room temperature, it was filtered under nitrogen. In the absence of air the lustrous, dark purple, crystalline needles were washed well with benzene, sparingly with chloroform and acetone, and finally with several portions of diethyl ether. The product was then dried in nitrogen to give about a 40% yield of CrPc.

Anal. Calcd for $C_{32}H_{16}CrN_8$: C, 68.08; H, 2.86; Cr, 9.21; N, 19.85. Found: C, 68.17; H, 4.27; Cr, 9.4; N, 19.61.

In air this product readily oxidizes to CrPcOH.

Anal. Calcd for $C_{32}H_{17}CrN_8O$: C, 66.09; H, 2.95; N, 19.27. Found: C, 66.23; H, 2.95; N, 19.31.

Other Known Phthalocyaninato(2−)chromium(III) Derivatives.—Portions of CrPcOH were converted to $CrPcOOCCH_3$ and $CrPc(CH_3OH)_2OH$ by the procedures of Elvidge and Lever,[2] and a sample of CrPcOH was converted to $CrPc(H_2O)_2OH$ by treatment with refluxing 95% ethanol for several hours. Elemental analyses were in agreement with those reported by Elvidge and Lever.

Phthalocyaninato(2−)chromium(III) Phosphinates.—Refluxing a mixture of CrPcOH and a phosphinic acid in methanol for several hours yielded a green solid which was filtered out of the mixture and washed thoroughly with methanol to remove excess phosphinic acid. After the products were dried, they analyzed as dimethanol adducts of the appropriate phthalocyaninato(2−) phosphinates. Analytical data are recorded in Table I.

The dimethyl- and diphenylphosphinate adducts were heated to constant weight at 180° and 15 torr. Analytical data, indicating loss of only 1 mole of methanol, are given in Table II.

In an additional attempt to isolate an unsolvated phosphinate, CrPcOH was refluxed overnight in chloroform with excess $CH_3(C_6H_5)P(O)OH$. Filtration, washing with chloroform and di-

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[1] To whom inquires should be addressed.

[2] J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, 1257 (1961).

[3] Pc will be used throughout to represent the phthalocyanine anion $C_{32}H_{16}N_8^{2-}$ as has become customary.

[4] A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 52 (1965).

[5] R. D. Joyner, R. G. Linck, J. N. Esposito, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **24**, 299 (1962); W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, *Inorg. Chem.*, **2**, 1064 (1963); and earlier papers.

[6] S. H. Rose and B. P. Block, *J. Polymer Sci.*, **A1**, 4, 583 (1966), and earlier papers.

[7] A. J. Saraceno and B. P. Block, *Inorg. Chem.*, **3**, 1699 (1964).

[8] L. C. Craig and D. Craig in "Technique of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1950, p 238.