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_{hkl}	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.

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
TECHNOLOGICAL CENTER,
KING OF PRUSSIA, PENNSYLVANIA 19406

Phthalocyaninato(2—)chromium(III) Phosphinates

BY E. G. MELONI, L. R. OCONE, AND B. P. BLOCK[1]

Received September 15, 1966

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 This structure (recently withdrawn by one of the authors[4]), the evidence Kenney and his coworkers have collected for the polymeric nature of several phthalocyanine derivatives of group IVb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$_3$OH)$_2$OH by the procedures of Elvidge and Lever,[2] and a sample of CrPcOH was converted to CrPc(H$_2$O)$_2$OH 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$_6$H$_5$)P(O)OH. Filtration, washing with chloroform and di-

---

[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.

TABLE I

ANALYTICAL DATA FOR $CrPc(CH_3OH)_2(OPRR'O)$

		% calcd					% found				
R	R′	C	H	Cr	N	P	C	Cr	N	N	P
CH_3	CH_3	59.92	4.19	7.21	15.53	4.29	60.08	4.48	7.4	15.39	4.15
CH_3	C_6H_5	62.83	4.12	6.63	14.30	3.95	63.46	4.00	...	14.68	3.83
C_6H_5	C_6H_5	65.32	4.05	6.15	13.25	3.66	65.23	3.89	6.3	13.07	3.72

TABLE II

ANALYTICAL DATA FOR SAMPLES OF $Cr(Pc)(CH_3OH)_2(OPRR'O)$ AFTER HEATING

		% calcd for loss of one CH_3OH					% found				
R	R′	C	H	Cr	N	P	C	H	Cr	N	P
CH_3	CH_3	60.96	3.80	7.54	16.25	4.49	61.15	3.60	7.5	16.20	4.30
C_6H_5	C_6H_5	66.41	3.72	6.39	13.77	3.81	66.18	3.76	6.4	13.38	3.51

ethyl ether, and drying yielded a green solid corresponding to $CrPc(H_2O)[OP(CH_3)(C_6H_5)O]$.

Anal. Calcd for $C_{39}H_{26}CrN_8O_3P$: C, 63.50; H, 3.55; Cr, 7.04; N, 15.19; P, 4.20. Found: C, 63.58; H, 3.51; Cr, 7.4; N, 15.09; P, 4.43.

FePc.—A solution of 8.0 g of phthalonitrile in 100 ml of 1-chloronaphthalene was heated to reflux under nitrogen with stirring, and then a solution of 3.0 g of $Fe(CO)_5$ in 50 ml of 1-chloronaphthalene was slowly added from a separatory funnel. Refluxing was continued 30 min after the addition was complete. The cooled mixture was filtered, and the insoluble product was washed with benzene, chloroform, acetone, and diethyl ether and dried; yield of FePc, 4.3 g (50%).

Anal. Calcd for $C_{32}H_{16}FeN_8$: C, 67.62; H, 2.84; Fe, 9.83; N, 19.71. Found: C, 67.6; H, 2.8; Fe, 10.1; N, 19.6.

Spectra.—Infrared spectra were determined for Nujol mulls on a Perkin-Elmer Model 221 instrument. The lines common to the spectra were in basic agreement with those reported earlier,[2] the most notable difference being the presence of a line of medium intensity at 1485 ± 4 cm^{-1} in all of our spectra. Additional bands (cm^{-1}) were observed as follows for the phosphinates: common: 1176 w sh, 1000 ± 4 m, 801 ± 1 w; $CrPc(CH_3OH)[OP(CH_3)_2O]$: 1294 m, 1103 s, 979 w, 944 w, 869 m, 854 m; $CrPc(CH_3OH)_2[OP(CH_3)_2O]$: 1294 m, 979 w, 948 w, 869 m, 856 w; $CrPc(CH_3OH)[OP(C_6H_5)_2O]$ and $CrPc(CH_3OH)_2[OP(C_6H_5)_2O]$: 1015 w, 944 ± 1 w, 847 w, 720 ± 2 sh, 692 m; $CrPc(CH_3OH)_2[OP(CH_3)(C_6H_5)O]$: 1127 sh, 1025 w, 972 w, 943 w, 868 w, 690 m; $CrPc(H_2O)[OP(CH_3)(C_6H_5)O]$: 1127 sh, 1025 w, 960 w, 870 m, 690 m. Our spectra for CrPcOH, $CrPc(H_2O)_2OH$, and $CrPc(CH_3OH)_2OH$ were in substantial agreement with those of Elvidge and Lever.[2]

Thermogravimetric Analysis.—Thermogravimetric studies were made on a modified Chevenard thermobalance[9] at a heating rate of 5°/min in nitrogen. For $CrPc(CH_3OH)_2[OP(C_6H_5)_2O)]$, initial weight loss starts at 150° and levels off at 3.6% at 325°. Catastrophic weight loss then starts at about 470° (24.1% to next plateau). Weight loss calculated for loss of one CH_3OH is 3.79%; for two, 7.58%. For $CrPc(CH_3OH)_2[OP(CH_3)_2O]$ initial weight loss starts at about 70° and levels off at 4.8% at about 120°. Catastrophic weight loss then starts at about 460° (run terminated at 660° with a 20% weight loss). Weight loss calculated for loss of one CH_3OH is 4.44%; for two, 8.88%.

Discussion

The preparation of CrPc and FePc from the reactions in high-boiling solvents of phthalonitrile with $Cr(CO)_6$ and $Fe(CO)_5$, respectively, has proved very convenient for small-scale work. Precipitation of the phthalocyanine derivatives from a homogeneous reaction medium yields good quality products which do not have to be sublimed away from contaminants for purification. The compound CrPc is a very useful intermediate for the preparation of chromium(III) derivatives of phthalocyanine, for exposure to air converts it quantitatively to CrPcOH.

We were unable to elicit evidence for polymeric chromium(III) phthalocyanine phosphinates. Although the species $CrPc(CH_3OH)_2(OPRR'O)$ and $CrPc(CH_3OH)(OPRR'O)$ were readily made and simple heating converted the former to the latter by loss of CH_3OH, continued heating of the latter ultimately led to extensive decomposition with no indication for simple loss of the second CH_3OH. Furthermore, when CrPcOH was treated with methylphenylphosphinic acid in chloroform, the 1 mole of water formed was all incorporated into the product $CrPc(H_2O)[PO(CH_3)(C_6H_5)O]$. In addition to the experiments described directed toward the preparation of CrPc(OPRR′O), other approaches were investigated. Use of higher temperatures in solvents boiling higher than chloroform also yielded $CrPc(H_2O)(OPRR'O)$, the substitution of $CrPcOOCCH_3$ for CrPcOH failed, and the reaction of CrPc with RR′P(O)OH did not give the desired product. This failure to form species of the type CrPc(OPRR′O) is somewhat surprising in view of the relatively straightforward preparation of $CrPcOOCCH_3$. Models suggest that the phosphinate groups cannot be bonded to two $CrPc^+$ units for steric reasons, so that polymer formation is not likely. However, there is no apparent reason for our inability to isolate the unsolvated phosphinates.

Detailed assignment of the infrared spectra of metal derivatives of phthalocyanine has not yet been made, so that pertinent information cannot be gleaned from the spectra. In fact, the bands common to all the chromium derivatives of phthalocyanine do not appear diagnostic, for they are found in the spectra of other metallic derivatives of phthalocyanine as well.[10]

Acknowledgment.—This work was supported in part by the Office of Naval Research. We are indebted to W. E. Smith for experimental assistance, Miss Ruth Kossatz for the infrared study, Dr. J. R. Soulen for the tga results, and our analytical department for the elemental analyses.

---

(9) J. R. Soulen and I. Mockrin, *Anal. Chem.*, **33**, 1909 (1961).

(10) Reference 4, pp 86–89.