in fused $HgCl_2$ decreased linearly on addition of NaCl until the mole ratio $Hg(ClO_4)_2$:2NaCl was reached. Thereafter the conductivity of the solution increased rapidly.

Solutions of $Hg(NO_3)_2$ in fused $HgCl_2$ could not be prepared. When $Hg(NO_3)_2 \cdot H_2O$ was dissolved in the melt, rapid evolution of NO_2 occurred.

A 0.1 *M* solution of acridine showed an equivalent conductivity of 100 mhos cm.^{2} equiv.$^{-1}$. Solutions of acridine in $HgCl_2$ gave, after extraction of excess $HgCl_2$ with ether, green needles with the composition $1C_{13}H_9N \cdot 3HgCl_2$.

Discussion

Because of the close chemical and physical resemblance of mercuric bromide and mercuric chloride, a similarity of the acid–base reactions in both systems can be expected. Table I shows that in principle this is the case. $Hg(ClO_4)_2$, $Hg(NO_3)_2$, and $HgSO_4$ acted as acids in both solvent systems. Alkali and heavy metal bromides in fused $HgBr_2$ and alkali and heavy metal chlorides in fused $HgCl_2$ acted as bases, forming the corresponding salts in neutralization reactions. It is also evident from the table that some conductometric titration curves exhibited several breaks corresponding to different acid–base mole ratios. These breaks can be attributed to the formation of neutral salts and of acid salts which are thought to contain HgBr and HgCl groups. In addition to these similarities we found some differences between acid–base reactions in both solvent systems; moreover, we performed some other types of reactions which were not done in fused $HgBr_2$.

Although the titration curves obtained by using fused $HgBr_2$ as the solvent indicated the formation of acid salts, these salts could not be isolated from the melt. In all instances the acid salts decomposed and gave salts which did not contain bromine. In the case of $HgCl_2$, however, chlorine-containing salts could be isolated, for example, $3TlCl \cdot 3HgSO_4 \cdot 2HgCl_2$. Since the results in Table I show that $HgSO_4$ is a dibasic acid in fused $HgCl_2$ and since the base:acid mole ratio in $3TlCl \cdot 3HgSO_4 \cdot 2HgCl_2$ is 1:1, this compound can be considered an acid salt and thus be formulated as $3Tl(HgCl)SO_4 \cdot 2HgCl_2$. In a few instances, the acid salts in $HgCl_2$ were unstable and behaved like the acid salts in the $HgBr_2$ system. For example, in the case of $Na(HgCl)SO_4$, decomposition occurred yielding $Na_2SO_4 \cdot HgSO_4$ and $HgCl_2$.

The high equivalent conductivity of solutions of $Hg(ClO_4)_2$ and the shape of the conductometric titration curves obtained by titration with NaCl (see Results section) showed that $Hg(ClO_4)_2$ was the strongest of the acids investigated. $Hg(ClO_4)_2$ was likewise the strongest acid in fused $HgBr_2$. The decrease in conductivity of solutions of $Hg(ClO_4)_2$ in fused $HgCl_2$ and the change in the equivalence point on titration with NaCl with time (see Results section), however, indicate that solutions of $Hg(ClO_4)_2$ in fused $HgCl_2$ were not stable over long periods of time. Solutions of $Hg(ClO_4)_2$ in $HgBr_2$ were stable. Solutions of $Hg(NO_3)_2$ were likewise stable in fused $HgBr_2$ and unstable in fused $HgCl_2$. Since the experiments in fused $HgCl_2$ were performed at a 40° higher temperature than those in fused $HgBr_2$, it is reasonable to assume that decomposition of the $Hg(ClO_4)_2$ and $Hg(NO_3)_2$ in fused $HgCl_2$ resulted from the higher temperature.

Despite the instability of $Hg(NO_3)_2$ solutions in fused $HgCl_2$, it was possible to interact $Hg(NO_3)_2$ with alkali chlorides, but only when the alkali chlorides were titrated with the acid (Table I). Under these conditions, the $Hg(NO_3)_2 \cdot H_2O$ reacted immediately with the alkali chloride forming the corresponding salt while the crystal water evaporated.

Acridine behaved as a base in the $HgCl_2$ melt and its solutions showed a high conductivity. Moreover, its compounds isolated from the $HgCl_2$ melt contained solvent molecules (see Results section). Investigations of other nonaqueous systems such as fused $AsBr_3$[8] have shown that some aliphatic and aromatic amines behave similarly in these systems. This behavior probably results from the lone electron pair of the nitrogen in these substances causing an affinity to electropositive groups.

With NaCl, $PbCl_2$ acted as an acid in fused $HgCl_2$; with $HgSO_4$ it behaved as a base (Table I). This behavior illustrates the amphoteric character of $PbCl_2$ in fused $HgCl_2$.

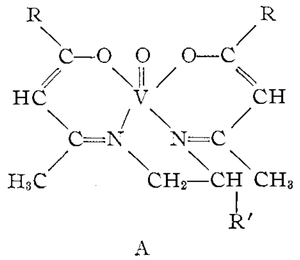
Contribution from the Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois

Preparation and Resolution of a Five-Coordinate Complex: Bisacetylacetonepropylenediiminooxovanadium(IV)

By K. Ramaiah, F. E. Anderson, and Dean F. Martin

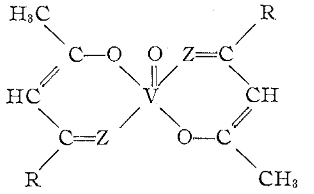
Received September 13, 1963

Recent structural analysis of bis(2,4-pentanediono)oxovanadium(IV)[1] has established that this compound is an example of a five-coordinate complex and that the structure is nearly square pyramidal. It seemed likely that related compounds of type A and B might



A

R = CH_3, R′ = CH_3



B

R = CH_3, Z = NR′
R = C_6H_5, Z = O

---

(1) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

TABLE I

CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF COMPOUND I

Solute adsorbed, g.	Chromatographic conditions	Quantity recovered, g.[a]	Active eluted fractions: Concn., 10^2 M	Specific rotation, $[\alpha]_{5983}$[b]	Max. mol. rotation, $[M]_{5983}$[c]	Racemization constant, 10^2k, hr.$^{-1}$
0.0490	Column: 13 drops/min.	0.0460	1.044	−6.63	−20.11	
	Breakthrough: 9.25 hr.					3.2
	Total time: 12.00 hr.		1.102	+6.89	+20.89	
0.0569	Column: 12 drops/min.	0.0530	0.664	−12.43	−37.69	
	Breakthrough: 8.0 hr.					3.9
	Total time: 11.0 hr.		0.711	+11.59	+35.15	

[a] Determined spectrophotometrically. [b] Readings determined using a Bendix Ericsson ELT-NPL automatic polarimeter, Type 143A, and a 4.0-cm. cell (precision = ±0.0004°). [c] $[M]_{5983} = [\alpha]_{5983} \times$ molecular weight $\times 10^{-2}$.

also have a square pyramidal structure and would exhibit stereoisomerism. Compounds of type A should exist as optical enantiomers. Compounds of type B should exhibit both geometrical and optical isomerism; the *trans* forms should be susceptible to resolution into optical enantiomers.

A compound of type A, bisacetylacetonepropylenediiminooxovanadium(IV), compound I, was prepared by heating the ligand[2] (0.012 mole) and bis-(2,4-pentanediono)oxovanadium(IV) hydrate (0.01 mole) at 230–250° for 2.5 hr.; acetylacetone distilled, and the product was isolated from the residue by crystallization from toluene: dark blue crystals, m.p. 199–200° (24% yield). *Anal.* Calcd. for $C_{13}H_{20}O_3N_2V$: C, 51.48; H, 6.60; N, 9.24. Found: C, 51.56; H, 6.54; N, 9.09.[3]

Compound I was resolved by means of a chromatographic technique[4] which consisted of adsorption on a column of D-lactose, followed by elution with toluene. Prior to adsorption, there was no indication of optical activity of compound I in toluene. Typical resolution data are summarized in Table I. Concentrations of the eluted fractions were determined spectrophotometrically, and it was found that the spectra of the eluted fractions corresponded to those of compound I.

Compound I should exist as two pairs of optical enantiomers inasmuch as the ligand itself contains an asymmetric carbon atom. In each trial only two fractions having maximum dextro and levo rotation were observed. However, it has been found that either fraction undergoes slow mutarotation, reaches a maximum value, and then racemization apparently occurs. This is a stereospecific change, and it is provisionally interpreted as being due to conversion of a less stable enantiomorphic form to the more stable, followed by racemization. However, because of the low magnitude of the specific rotation, it has not been possible to determine the rotatory dispersion curves.

It should be noted that compound I could be a six-coordinate complex in solution with a molecule of toluene occupying the sixth coordination position. It has not been possible to detect the formation of a toluene adduct in carbon tetrachloride solution as determined by Job's method[5] using absorption spectra (380–720 mμ).

Investigation of the optical activity of compounds of type A and B is in progress.

Acknowledgment.—This investigation was supported by P.H.S. Research Grant 7873, Division of General Medical Sciences, U. S. Public Health Service.

---

[2] P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).

[3] A second sample was prepared by heating the ligand[2] (0.01 mole) and vanadium pentoxide (0.014 mole) at 240° for 1.2 hr.; dark blue crystals, m.p. 202–204°. *Anal.* Found: C, 51.39; H, 6.66; N, 8.98.

[4] T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958).

[5] *Cf.* W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

CONTRIBUTION FROM INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD, ENGLAND

The Preparation of Hexaborane

BY P. L. TIMMS[1] AND C. S. G. PHILLIPS

Received August 30, 1963

Hexaborane has long been one of the least accessible of the boron hydrides, being first isolated by Stock[2] in poor yield by the hydrolysis of magnesium boride, and more recently by Kotlensky and Schaeffer,[3] by the action of an electrical discharge on diborane, and by Boone and Burg[4] in good yield by treating unstable pentaborane B_5H_{11} with bases.

We have hydrolyzed magnesium boride prepared from technical amorphous boron and magnesium powder and have found the yields of hexaborane to be at least ten times as high as reported by Stock or by the Russian workers Markina and Mikheeva.[5] The mixture of hydrides obtained by the hydrolysis was separated by gas–liquid chromatography, and the individual hydrides were trapped and weighed to determine the yields. The hexaborane was identified by its molecular weight[6] (found 75.5, correct 74.9),

---

[1] Author to whom communications should be addressed at the Department of Chemistry, Rice University, Houston 1, Texas.

[2] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[3] W. V. Kotlensky and R. Schaeffer, *J. Am. Chem. Soc.*, **80**, 4517 (1958).

[4] J. L. Boone and A. B. Burg, *ibid.*, **80**, 1519 (1958); **81**, 1766 (1959).

[5] V. I. Mikheeva and V. Yu. Markina, *Zh. Neorgan. Khim.*, **1**, 619 (1956).

[6] C. S. G. Phillips and P. L. Timms, *J. Chromatog.*, **5**, 131 (1961).