

## NOTE

## Synthesis and Structural Investigations of Some Five-coordinated Oxovanadium(IV) Complexes of 4[N-(Benzylidene)amino] Antipyrine Semicarbazone

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The synthesis and spectral characteristics of a new series of five coordinated oxovanadium(IV) complexes of 4[N-(benzylidene)antipyrine semicarbazone (BAAPS) with general composition  $VOX_2 \cdot BAAPS$  ( $X = Cl, Br, I, NO_3$  or  $NCS$ ) and  $VO(ClO_4)_2 \cdot BAAPS \cdot H_2O$  are reported together with molecular conductivity, molecular weights, magnetic susceptibility, infrared and electronic spectra. In all the complexes, the BAAPS behaves as neutral tridentate (N,N,O) ligand.

In the past Agarwal and Chakraborti have reported the oxovanadium(IV) complexes of various Schiff bases and thiosemicarbazones.<sup>1-4</sup> As a part of the coordination chemistry of oxocations, in the present communication we report some new coordination compounds of oxovanadium(IV) with 4[N-(benzylidene)-amino] antipyrine semicarbazone (BAAPS).

Oxovanadium(IV) chloride and oxovanadium(IV) bromide were prepared from  $V_2O_5$  and other salts were prepared as reported earlier<sup>1-4</sup>. The ligand BAAPS was synthesized by refluxing an ethanolic solution of 1 : 1 : 1 molar ratio of 4-aminoantipyrine benzaldehyde and neutralised<sup>5</sup> semicarbazide hydrochloride for ca. 2h. On cooling the ligand BAAPS was precipitated out. It was filtered, washed with ethanol, ether and dried in vacuum in a desiccator over  $P_4O_{10}$  (yield ca. 75%, m.f.  $C_{19}H_{20}N_5O$ ).

All the complexes were synthesized by the following general method. To a hot solution of the respective oxovanadium(IV) salt in ethanol, a sufficient amount of 2,2'-dimethoxy propane (a dehydrating agent) was added. This solution was mixed with a stoichiometric amount of the ligand in hot ethanol.<sup>5</sup> The resulting mixture was refluxed for about 30 min and then concentrated to half of its volume. On cooling, crystalline products were obtained which were filtered, washed with organic solvents and dried in vacuum desiccator over  $P_4O_{10}$ .

Vanadium in the complexes was estimated as  $V_2O_5$  while the other physico-chemical techniques were the same as described earlier.<sup>1-4</sup>

The analytical data on the complexes are presented in Table 1. The molar

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conductances measured in nitrobenzene are consistent with the non-electrolytic nature of halo, pseudohalo and nitrate complexes, while the perchlorate complex is a 1 : 2 electrolyte. The molecular weight data also support the similar behaviour. The magnetic moments of the present complexes were found to be in 1.67–1.74 B.M. range (Table-1). These magnetic moments are close to spin-only value expected for  $3d^1$  VO(IV) complexes with normal magnetic properties.<sup>1-4, 6</sup>

TABLE I  
ELEMENTAL ANALYSIS, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC SUSCEPTIBILITY DATA OF OXOVANADIUM(IV) COMPLEXES OF BAAPS

Complex	Found (Calcd.) %			Mol. Wt. Exp. (Calcd.)	$\Omega_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> )	$\mu_{eff}$ (B.M.)
	V	N	Anion			
VOCl <sub>2</sub> ·BAAPS	10.88 (10.80)	14.94 (14.83)	15.15 (15.04)	467 (472)	3.6	1.71
VOBr <sub>2</sub> ·BAAPS	9.17 (9.09)	12.58 (12.47)	28.67 (28.52)	557 (561)	3.9	1.69
VOI <sub>2</sub> ·BAAPS	7.86 (7.78)	10.77 (10.68)	38.59 (38.77)	649 (655)	4.1	1.74
VO(NO <sub>3</sub> ) <sub>2</sub> ·BAAPS	9.78 (9.71)	18.77 (18.66)	— —	519 (525)	2.9	1.67
VO(NCS) <sub>2</sub> ·BAAPS	9.94 (9.86)	19.09 (18.95)	22.36 (22.43)	509 (517)	3.3	1.72
VO(ClO <sub>4</sub> ) <sub>2</sub> ·BAAPS·H <sub>2</sub> O	8.32 (8.25)	11.43 (11.32)	32.08 (32.20)	203 (618)	52.42	1.74

The partial infrared spectral data of the BAAPS and its VO<sup>2+</sup> complexes are given in Table-2. As expected, the  $\nu(\text{NH}_2)$  band of the hydrazinic nitrogen of semicarbazide (1622 cm<sup>-1</sup>) is absent in the infrared spectra of the semicarbazone.<sup>7</sup> It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen.<sup>8</sup> The characteristic absorption of the carbonyl group in BAAPS is observed<sup>9</sup> at 1700 cm<sup>-1</sup>. In the complexes this band is shifted towards lower energy in the 1650–1640 cm<sup>-1</sup> region. The amide-II band in the free ligand has been observed at 1565 cm<sup>-1</sup>. In all the present complexes this band is also shifted towards lower wave numbers. This observation suggests coordination through the carbonyl-oxygen atom. The strong band at 1600 cm<sup>-1</sup> in BAAPS, apparently has a large contribution from the  $\nu(\text{C}=\text{N})$  band<sup>10</sup> of semicarbazone moiety. This has been observed as a blue-shift in the position of the (C=N) band in all complexes as compared to the ligand. Another strong band was observed at ca.1610 cm<sup>-1</sup> due to the azomethine (C=N) absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N-atom.<sup>1-3</sup>

TABLE 2  
KEY IR BANDS ( $\text{cm}^{-1}$ ) of  $\text{VO}^{2+}$  COMPLEXES OF BAAPS

Compound	$\nu(\text{C}=\text{N})$ (azo- methinic)	$\nu(\text{C}=\text{N})$ (hydra- zinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{V}=\text{O})$ (Oxo- cation)	$\nu(\text{V}-\text{O})/$ $\nu(\text{V}-\text{N})$
			I	II	III		
BAAPS	1610s	1600 s	1700 s	1565 m	1350 m	—	—
$\text{VOCl}_2 \cdot \text{BAAPS}$	1585 s	1625 s	1640 s	1530 m	1335 m	970 w	440 m 385 w
$\text{VOBr}_2 \cdot \text{BAAPS}$	1582 s	1628 s	1650 s	1525 m	1340 m	935 m	420 m 375 w
$\text{VOI}_2 \cdot \text{BAAPS}$	1580 s	1630 s	1650 s	1532 m	1332 m	955 m	435 m 390 w
$\text{VO}(\text{NO}_3)_2 \cdot \text{BAAPS}$	1590 s	1632 s	1645 s	1530 m	1335 m	965 m	410 m 360 w
$\text{VO}(\text{NCS})_3 \cdot \text{BAAPS}$	1585 s	1630 s	1640 s	1528 m	1333 m	950 m	435 m 385 w
$\text{VO}(\text{ClO}_4)_2 \cdot \text{BAAPS} \cdot \text{H}_2\text{O}$	1582 s	1630 s	1645 s	1530 m	1335 m	960 m	430 m 380 w

In the nitrate complex, the absence of the  $\nu_3$  bands of ionic nitrate ( $D_{3d}$ ) around  $1360 \text{ cm}^{-1}$  and the occurrence of two strong bands at *ca.*  $1500$  and  $1300 \text{ cm}^{-1}$  due to the split of the  $\nu_3$  mode in the lower symmetry indicate a coordinated nitrate group.<sup>11</sup> By applying Lever's separation method, a separation of *ca.*  $25 \text{ cm}^{-1}$  in combination bands ( $\nu_1 + \nu_4$ ) ( $1760$  and  $1735 \text{ cm}^{-1}$ ) concludes the monodentate nitrate coordination.<sup>12</sup> Other bands, at *ca.*  $1030$  ( $\nu_2$ ),  $810$  ( $\nu_6$ ) and  $730 \text{ cm}^{-1}$  ( $\nu_3/\nu_5$ ) due to nitrate groups are also identified. In the perchlorato complex, the  $\nu_3$  and  $\nu_4$  bands of the perchlorato group appear at *ca.*  $1100$  and  $625 \text{ cm}^{-1}$  respectively. This indicates that the  $T_d$  symmetry has not been disturbed in this complex and both the perchlorato ions are present outside the coordination sphere.<sup>13</sup> The thiocyanate complex shows three bands at *ca.*  $2040$ ,  $855$  and  $465 \text{ cm}^{-1}$  assignable to  $\nu(\text{CN})$ ,  $\nu(\text{CS})$  and  $\delta(\text{NCS})$  vibrations, respectively in the case of N-coordinated isothiocyanate groups.<sup>14</sup> In oxovanadium(IV) perchlorato complex, the presence of coordinated water was suggested by the very broad absorption centred around  $3450 \text{ cm}^{-1}$  in the IR-spectra. Bands at *ca.*  $930$  and  $770 \text{ cm}^{-1}$  may be attributed to rocking and wagging modes of the coordinated water.

In all the  $\text{VO}^{2+}$  complexes, the  $\text{V}=\text{O}$  stretching frequency occurs, in the  $970\text{--}935 \text{ cm}^{-1}$  region due to monomeric nature of these complexes.<sup>1-4</sup>

In general,  $\text{VO}^{2+}$  complexes display three low intensity bands in the  $10,000\text{--}30,000 \text{ cm}^{-1}$  range (Table-3). According to Ballhausen and Gray scheme, the first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond  $30,000 \text{ cm}^{-1}$ ) and often band-III is not observed but is believed buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels (BG scheme), the first shoulder which is

centred at about 13,000  $\text{cm}^{-1}$  is assigned to an unresolved band resulting from the  $d_{xy} \rightarrow d_{xz} \rightarrow d_{yz}$  ( ${}^2B_2 \rightarrow {}^2E$ ) transition. The second band (in 16,900–17300  $\text{cm}^{-1}$ ) is attributed to  $d_{xy} \rightarrow d_{x^2-y^2}$  ( ${}^2B_2 \rightarrow {}^2B_1$ ) transitions. The band at about 25,000  $\text{cm}^{-1}$  may either be assigned to the  $d_{xy} \rightarrow d_{z^2}$  ( ${}^2B_2 \rightarrow {}^2A_1$ ) transition or believed to be low energy charge-transfer band.

TABLE 3  
ELECTRONIC SPECTRAL BANDS ( $\text{cm}^{-1}$ ) OF  $\text{VO}^{2+}$  COMPLEXES OF BAAPS

Complex	Band-I $d_{xy} \rightarrow d_{xz}, d_{yz}$	Bond-I $d_{xy} \rightarrow d_{x^2-y^2}$	Band-III $d_{xy} \rightarrow d_{z^2}$
$\text{VOCl}_2 \cdot \text{BAAPS}$	13,500	17,200	24,000
$\text{VOBr}_2 \cdot \text{BAAPS}$	13,000	16,900	24,900
$\text{VOI}_2 \cdot \text{BAAPS}$	13,300	17,250	—
$\text{VO}(\text{NO}_3)_2 \cdot \text{BAAPS}$	12,900	17,300	25,000
$\text{VO}(\text{NCS})_2 \cdot \text{BAAPS}$	13,100	17,000	24,600
$\text{VO}(\text{ClO}_4)_2 \cdot \text{BAAPS} \cdot \text{H}_2\text{O}$	13,200	17,000	—

In conclusion, due to steric interactions of the larger size of the ligand the lower coordination number five has been assigned to these complexes. The five coordinated complexes of  $\text{VO}^{2+}$  may have the usual tetragonal pyramidal structure.<sup>16</sup>

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