Inorganica Chimica Acta, 118 (1986) 141–145

Synthesis of some Novel Transition Metal Complexes of Phosphoramidothioic and Phosphorodiamidothioic Ligands and Study of their Bonding Mode with CNDO/2 Calculations

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(Received February 3, 1986; revised April 17, 1986)

Abstract

New complexes of phosphoramidothioic and phosphorodiamidothioic ligands with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been synthesized and characterized The structure and bonding of the new compounds were established by spectroscopic methods (IR, UV–Vis) and magnetic susceptibility measurements. In an attempt to understand the bonding capacity of the ligands employed and the parameters of their bonding effects CNDO/2 calculations were performed.

Introduction

Although the phosphoramidothioic, $[PO_2S(NH_2)]^{2-}$, and phosphorodiamidothioic, $[POS(NH_2)_2]^-$, ligands are biologically important, acting as radioprotective agents [1–3], their electronic and bonding properties have not been studied thoroughly so far. The formation of some phosphorodiamidate complexes by the reaction of $PO(NH_2)_3$ with the alkali metal hydroxide has been reported [4–6]. Moreover, the complex of $(EtO)_2$-PSNHCSNHPh with Hg(II) has been synthesized [7] by the reaction of the HgO with the above ligand. Finally, some dialkyldithiophosphate complexes with various metal ions [8–16] have also been characterized. The salient feature of the reaction of the phosphoramidothioic and phosphorodiamidothioic ligands is the variety of possible stoichiometries and molecular geometries of the products formed, owing to the four possible coordinating sites of the aforesaid ligands. In order to expand the knowledge in this area we performed CNDO/2 calculations on the $[PO_2S(NH_2)]^{2-}$ and $[POS(NH_2)_2]^{1-}$ ligands and attempted to determine the parameters of the ligand bonding effects by means of some quantum chemical indices related to the frontier MOs [17]. Furthermore, we verified the theoretical expectations by the preparation and characterization of the corresponding complexes with transition metal ions, such as Mn(II), Fe(III), Co(II), Ni(II) and Cu(II). Consequently, the results of our attempts to estimate quantitatively the bonding capacities of the ligating atoms on the free anions as well as the synthesis and study of some novel complexes with open-shell transition metal atoms are reported in this paper.

Experimental

Physical Measurements

Infrared spectra were recorded with KBr discs on a Perkin-Elmer 467 spectrophotometer (over the range 4000–250 cm^{-1}). Electronic spectra were obtained with a Cary 17DX spectrophotometer and in a Perkin-Elmer Hitachi 200, in solid state with Nujol mulls. The H and N analyses were performed on a Perkin-Elmer 240 Elemental Analyser. The metal determinations were carried out volumetrically by published methods [18].

MO Calculations

All MO calculations were performed within the framework of CNDO/2 approximation [19]. Bond lengths and valence angles were obtained from X-ray structures of the ligands [20, 21].

Preparation of the Complexes

Both the ligands $[PO_2S(NH_2)]^{2-}$, $[POS(NH_2)_2]^-$ were prepared as described elsewhere [22]. The following general method is representative.

(a) Phosphoramidothioic Complexes $M[PO_2S(NH_2)](H_2O)_x$ or $M_2[PO_2S(NH_2)]_3(H_2O)_x$

To a solution of 2 mmol of a hydrated metal chloride in 20 ml of water, phosphoramidothioic ammonium (2.2 mmol), dissolved in water (20 ml), was added slowly and under constant stirring (2 h) at room temperature, affording a coloured residue. The precipitate was filtered off, washed with water,

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0020-1693/86/$3.50

ethanol and diethyl ether successively and dried *in vacuo* above P_2O_5 for 48 h. In the case of trivalent metals 3.3 mmol of ammonium salt were used.

(b) Phosphorodiamidothioic Complexes $M[POS(NH_2)_2]_2(H_2O)_x$ *or* $M[POS(NH_2)_2]_3(H_2O)_x$

They were prepared in a similar manner to that described above, the differences being the use of 4.4 mmol for either the ammonium salt or the metal chloride. In the case of trivalent metals 6.6 mmol of phosphorodiamidothioic ammonium was used. In order to complete the precipitation of the complexes, ethanol (40 ml) was added to the mother liquid.

Results and Discussion

The phosphoramidothioic ion reacts readily with the hydrated divalent and trivalent metals in 1:1 and 2:3 molar ratios, respectively, and gives coloured hydrated solid compounds of the types $M[PO_2S\text{-}NH_2)](H_2O)_x$ (M = Mn(II), Co(II), Ni(II), Cu(II)) and $M_2[PO_2S(NH_2)]_3(H_2O)_4$ (M = Fe(III)). The reaction of the phosphorodiamidothioic ion with the same hydrated metal chlorides also affords coloured, hydrated compounds of the type $M[POS(NH_2)_2]_2(H_2O)_x$ or $M[POS(NH_2)_2]_3(H_2O)_x$ in the case of trivalent metal ions. These complexes, which were obtained in 60/70% yields, were amorphous solids, air-stable, non conducting and paramagnetic. They were insoluble in water and in many common organic solvents, such as chloroform, acetone, methylene chloride, ethanol and diethyl ether.

To eliminate unlikely structures of the new complexes, it seemed interesting to estimate quantitatively, by means of quantum chemical calculations, the bonding capacities of each actual donor atom on the free ligand anions. Thus, we attempted to determine the parameters of the ligand bonding effects in terms of the atomic charges computed from the CNDO/2 eigenvectors by means of Mulliken's population analysis, as well as a number of well known quantum chemical indices derived from the density matrices and related to the frontier MOs.

All MO calculations were performed using the SCF-LCAO MO method within the CNDO/2 approximation [19] and were carried out for the anionic forms of the ligands, with actual geometries being those of their ammonium salts [20, 21] shown in Figs. 1a and 1b.

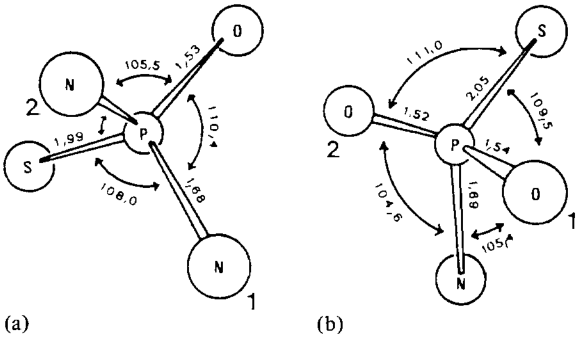

Fig. 1. (a) Phosphorodiamidothioic ion. (b) Phosphoramidothioic ion.

The energies and the composition (%) of the frontier occupied MOs for both investigated ligands are given in Table I. The HOMOs for both ligands are

TABLE I. The Composition (%) and the Eigenvalues (in a.u.) of the Frontier Orbitals of the Ligands

Ligand	MO-type	Eigenvalue	Eigenvectors			
			%P	%S	%OO	$\%NH_2$
$PO_2S(NH_2)^{2-}$	NNHOMO	0.0503	17.23	40.26	32.55	9.92
	NHOMO	0.0998	3.96	69.15	18.25	8.61
	HOMO	0.1187	0.27	66.64	32.97	0.09
	LUMO	0.6186	41.24	33.87	14.48	10.38
	NLUMO	0.6463	41.56	49.19	6.07	3.16
	NNLUMO	0.6591	37.48	48.15	12.24	2.10
			%P	%S	%O	$\%2NH_2$
$POS(NH_2)_2^{-}$	NNHOMO	−0.2353	22.39	49.68	15.99	11.92
	NHOMO	−0.1785	7.26	71.79	4.3	16.59
	HOMO	−0.1623	4.29	67.05	21.53	7.10
	LUMO	0.3364	42.76	31.25	8.79	17.17
	NLUMO	0.3601	44.50	46.07	4.70	4.69
	NNLUMO	0.3631	44.45	45.93	2.9	6.65

TABLE II. Electrofilicity Indices S_E for the Frontier Occupied MOs

	$POS(NH_2)_2^-$				$PO_2S(NH_2)^{2-}$		
	NNHOMO	NHOMO	HOMO		NNHOMO	NHOMO	HOMO
S	−2.111	−4.022	−4.131	S	8.006	6.929	5.615
O	−0.680	−0.242	−1.327	O_1	3.372	1.073	1.530
N_1	−0.181	−0.391	−0.197	O_2	3.100	0.757	1.198
N_2	−0.310	−0.496	−0.217	N	1.968	0.836	0.008

almost localized on the sulfur atom, whereas for the NHOMO and NNHOMO there exist a small delocalization to other atoms. The contribution of the atomic orbitals of all atoms to these MOs decreases in the order S > O > N so we can preliminarily conclude that the coordination to the metal ions takes place with an electron withdrawn from these MOs to the metal d AOs and consequently via the sulfur and oxygen atoms A stronger electron withdrawing ability of the [$POS(NH_2)_2$]$^-$ ligand is apparent from the increased electron density of its sulfur and oxygen atoms (Table I) as well as the highest energy of its frontier MOs in comparison with the corresponding MOs of the [$PO_2S(NH_2)$]$^{2-}$ ligand.

The computed values of some superdelocalizability indices, such as electrophilicity indices of the corresponding frontier orbitals [17], were proved eminently suitable for explaining the bonding capacities of coordinated atoms in each ligand. From the indices listed in Table II it is suggested that the greater values of the indices in going from [$POS(NH_2)_2$]$^-$ to [$PO_2S(NH_2)$]$^{2-}$ show the enhanced tendency for ligation of the latter ligand. Furthermore, the values of the indices for each atom indicate that strong coordination may take place through the sulfur atom and that the oxygen atoms are more likely to coordinate than the nitrogen ones. Coordination through the nitrogen atoms cannot be excluded in the case of dimeric or polymeric structures, especially since ligation of the sulfur and oxygen atoms engender redelocalization of the electron density on the ligand molecular fragment. Having all the above theoretical predictions in mind, we tried to establish the structure and bonding of the new complexes by spectroscopic methods (IR, UV–Vis) and magnetic susceptibility measurements.

The assignments of the main bands shown in the Table II were made based on the data reported previously for phosphorodiamidate salts [23, 24]. All the new hydrate compounds appearing in Table III exhibit a broad band in the 3420–3380 cm^{-1} region corresponding presumably to O–H stretching

TABLE III. Analytical Data[a] and Relevant IR Frequencies (cm^{-1}) of the New Phosphoramidothioic and Phosphorodiamidothioic Complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with their Assignments (KBr discs)[b]

Compound	%H	%N	%S	%M	$\nu(H_2O)$	$\nu(NH_2)$	$\delta(H_2O)$	ν(P–O)	ν(P–S)	ν(M–O)	ν(M–S)
[$Mn(PO_2SNH_2)(H_2O)_4$]	4.15	5.68	13.10	22.80	3420br	3180s	1630s	1130m	520m	432m	350s
	(4.23)	(5.88)	(13.47)	(23.08)				1050s			
[$Mn(POS(NH_2)_2)_2(H_2O)_2$]	3.80	17.00	19.80	16.80	3410br	3180m	1650m	1030s	550s	440m	350s
	(3.86)	(17.88)	(20.48)	(17.54)							
[$Fe_2(PO_2SNH_2)_3(H_2O)_4$]	2.72	8.00	17.90	20.98	3425br	3125m	1635m	1120m	530s	410m	350w
	(2.73)	(8.14)	(18.01)	(21.42)				1040vs			
[$Fe(POS(NH_2)_2)_3$]	2.95	20.88	24.30	13.80		3140m		1030s	550s	410s	360s
	(3.10)	(21.59)	(24.72)	(14.35)							
[$Co(PO_2SNH_2)(H_2O)_2$]	2.73	6.36	15.16	28.10	3400br	3200m	1640s	1095s	585m	465s	380w
	(2.93)	(6.79)	(15.60)	(28.60)				1055s			
[$Co(POS(NH_2)_2)_2$]	2.70	20.08	22.98	20.57		3220m		1150s	590s	460m	380w
	(2.86)	(19.92)	(22.81)	(20.96)							
[$Ni(PO_2SNH_2)(H_2O)_2$]	2.85	6.75	15.20	27.80	3370br	3270m	1630s	1145s	575s	460s	375w
	(2.93)	(6.80)	(15.97)	(28.52)				1085s			
[$Ni(POS(NH_2)_2)_2$]	3.11	19.88	22.60	20.20		3180m		1015s	560s	450s	380w
	(2.97)	(19.94)	(22.83)	(20.90)							
[$Cu_2(PO_2SNH_2)_2(H_2O)_2$]	1.98	7.00	16.30	32.00	3380br	3240w	1650s	1170s	550s	430m	360w
	(2.09)	(7.26)	(16.64)	(32.98)				1000m			
[$Cu(POS(NH_2)_2)_2(H_2O)_4$]	4.20	15.20	17.60	17.00	3380br	3200s	1630m	1180s	550s	425s	320w
	(4.50)	(15.65)	(17.92)	(17.76)				1010m			

[a] Figures in parentheses are the calculated values [b] vs = very strong, s = strong, m = medium w = weak, br = broad.

TABLE IV. Solid State Magnetic Moments and Electronic Spectral Data of the Phosphoramidothioic and Phosphorodiamidothioic Complexes of Mn(II), Fe(III), Co(II) Ni(II) and Cu(II)

Complex	μ_{eff} (BM)[a]	Electronic spectra × 10^3 (K)						10*Dq*	*B*	*β*
Manganese(II) complexes		$^4T_{1g}(G) \leftarrow {}^6A_{1g}$	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$	$^4A_{1g} \leftarrow {}^6A_{1g}$	$^4T_{2g}\,{}^4T_{2g}(D)$	$^4T_{1g} \leftarrow {}^6A_{1g}$	Other bands			
$Mn(PO_2SNH_2)(H_2O)_4$	5.89	18.5	23.0	25.8	28.0	32.0	44.4			
$Mn[POS(NH_2)_2](H_2O)_2$	5.90	18.3	22.6	25.0	27.5	31.6	44.0			
Iron(III) complexes		$^5T_{2g} \leftarrow {}^5E_g$								
$Fe_2(PO_2SNH_2)_3(H_2O)_4$	5.50	9.6sh					37.5, 27.0, 22.5, 17.6			
$Fe[POS(NH_2)_2]_3$	5.87	9.3sh					36.8, 26.0, 21.7, 17.3			
Cobalt(II) complexes		$^4T_1(P) \leftarrow {}^4A_2(F)$		$^4T_1(F) \leftarrow {}^4A_2(F)$						
$Co(PO_2SNH_2)(H_2O)_2$	4.67	16.0, 14.0sh		7.6			40.0, 35.5sh	4200	729	0.753
$Co[POS(NH_2)_2]$	4.60	16.0, 15.3, 14.6sh		7.4			39.0, 34.0sh	4110	737	0.762
Nickel(II) complexes		$^3T_1(P) \leftarrow {}^3T_1(F)$		$^3A_2(F) \leftarrow {}^3T_1(F)$						
$Ni(PO_2SNH_2)(H_2O)_2$	3.20	15.8, 14.9		7.9			44.5	4400	881	0.846
$Ni[POS(NH_2)_2]_2$	3.40	15.7, 14.7		7.8			43.6	4300	873	0.838
Copper(II) complexes		CT		$^2T_{1g} \leftarrow {}^2E_g$						
$Cu_2(PO_2SNH_2)(H_2O)_2$	1.30	23.2		15.6			41.6			
$Cu[POS(NH_2)_2(H_2O)_2]2H_2O$	1.33	22.3		14.9			40.8			

[a] Measured at room temperature.

vibrations [23–25]. Moreover, the absorption bands occurring in 3200–3100 cm^{-1} are characteristic of the N–H bond, [26, 27] and are shifted to higher frequencies relative to those of the free ligands. The absorption band at 1650–1630 cm^{-1} could be assigned to the bonding mode of the HOH, since it is absent from the anhydrous phosporodiamidate complexes [28]. The bands in the 1180–1000 cm^{-1} region are attributed to the stretching vibrations of the (P–O) bonds,, whereas the complexes of phosphoramidothioic ligand exhibit two bands attributable to stretching vibrations of the PO_2 group, which are also shifted to lower wavenumber in comparison with those of the free ligand. The bands in the 590–520 cm^{-1} region attributable to the stretching vibration of the P–S bond [24] are also shifted to lower frequencies. Finally, the bands observed in the 460–420 cm^{-1} and 380–320 cm^{-1} could be assigned to ν(M–O) and ν(M–S) vibrations, respectively [29–31].

The solid state magnetic moments and the electronic spectral data of the studied compounds are shown in Table IV. The optical spectra of Co(II) complexes are characteristic [32] for cobalt(II) compounds having a tetrahedral arrangement around the metal atom. They show two bands in the ranges 7800–7900 and 15 700–15 800 cm^{-1}, the latter also exhibits a shoulder at lower energies, corresponding to ν_2 $^4T_1(F) \leftarrow {}^4A_2(F)$ and to ν_3 $^4T_1(P) \leftarrow {}^4A_2(F)$, respectively. The adopted tetrahedral stereochemistry of the cobalt(II) complexes, was further supported by their observed μ_{eff} values lying in the range of 4.60–4.67 BM [33].

The μ_{eff} values of the nickel(II) complexes are between 3.20 and 3.40 BM and are indicative of tetrahedral nickel(II) stereochemistry [34]. The electronic spectra of Ni(II) complexes are very similar to those found for a variety of Ni(II) complexes with tetrahedral chromophores [35, 36]. The band at 15 700–15 800 cm^{-1} as well as the shoulder at 14 700–14 900 cm^{-1} can be assigned to ν_3 $^3T_1(P) \leftarrow {}^3T_1(F)$. There is also another moderately intense feature in the range 7800–7900 cm^{-1} which is presumably due to ν_2 $^3A_2(F) \leftarrow {}^3T_1(F)$. The most characteristic feature of the Fe(III) and Mn(II) complexes is their high-spin character which results in μ_{eff} values in the 5.6–5.8 and 5.8–5.9 BM ranges, respectively. Their electronic spectra are consistent with an octahedral structure [37]. The absorption spectra of Cu(II) complexes consist of a broad weak band at 15.0 kK attributed to the transition $^2T_{2g} \leftarrow {}^2E_g$ and another band which is due to charge transfer (CT) transitions [37]. The low values of the magnetic moment of the Cu(II) complexes lying at 1.30–1.33 BM (at room temperature) allows us to suggest that these complexes are dimeric rather than monomeric.

Finally, in the case of Co(II) and Ni(II) complexes the observed ligand-field bands allow us to calculate the parameters 10 *Dq*, *B* and *β*. The values found for these parameters are in accordance with those obtained from some tetrahedral complexes having ligands with sulfur or oxygen atoms as donors [34, 38].

Their IR data, the paramagnetic nature of the investigated complexes as well as their stoichiometry allowed us to propose the following structure: octahedral for the Mn(II) and Fe(III) complexes, tetrahedral for the complexes of Co(II), Ni(II) and an octahedral elongated square-planar for the Cu(II) complexes.

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