

## COMPLEXES OF N-METHYLIMINOBIS(METHYLENEPHOSPHONIC) ACID WITH COBALT, NICKEL, COPPER, AND ZINC

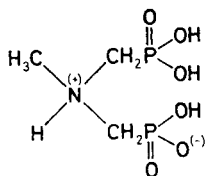
Ivan LUKEŠ, Zdeněk KVÁČA and Ivor DOMINÁK

*Department of Inorganic Chemistry, Charles University, 128 40 Prague 2*

Received June 2nd, 1987

The 1 : 1 cobalt, nickel, copper and zinc complexes of N-methyliminobis(methylene phosphonic) acid, and 1 : 2 cobalt and nickel complexes were prepared. The effect of alkali and alkali earth metals as "external cations" on the crystallization and stoichiometry of solid cobalt complex was investigated. Infrared and electronic spectra and magnetic susceptibilities indicate that cobalt and nickel form high-spin complexes. The coordination sphere of the central atom is formed by a distorted octahedron of the ligand oxygen atoms.

Aminoalkylphosphonic acids are interesting as analogues of natural amino acids and as chelating agents. Therefore, the principal interest has been centred on the complexing properties of these substances in solution. Coordination compounds of aminoalkylphosphonic acids in the solid state have been relatively little studied. The reason for this is the extraordinary solubility of coordination compounds in the form of acids and their alkali metal salts<sup>1-3</sup>, and the consequent difficulty of obtaining good-quality crystalline products. Therefore, only a few substances have been studied by X-ray analysis<sup>4,5</sup>. In an earlier work<sup>1</sup>, we prepared complexes of nitrilotrimethylenephosphonic acid ( $H_6ntmp$ ) with transition metals and studied the effect of external cations.  $Mg^{2+}$  was found to be the most convenient external ion, because of its weak complexing ability towards the ligand. As a continuation of our investigation of the complexing properties of N-methyliminobis(methylene-



phosphonic) acid ( $H_4mibmp$ ) in solution<sup>6</sup>, we now report the results of a study on the preparation and properties of cobalt, nickel, copper and zinc complexes with  $H_4mibmp$  in the solid state.

## EXPERIMENTAL

## Preparations

N-Methyliminobis(methylenephosphonic) acid was prepared by Mannich synthesis<sup>6,7</sup> from phosphorous acid, methylamine and formaldehyde in 20% HCl medium.

$[\text{MH}_2(\text{mibmp})]_n \cdot \text{H}_2\text{O}$  ( $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$ ). A solution of 30 mmol  $\text{H}_4\text{mibmp}$  in  $50 \text{ cm}^3$  water was added to a suspension of 30 mmol of freshly precipitated and washed transition metal hydroxide in  $100 \text{ cm}^3$  water. The resulting solution was filtered and evaporated to half-volume.  $[\text{CuH}_2\text{mibmp}] \cdot \text{H}_2\text{O}$  precipitated upon standing for several days. The other substances were isolated only after transferring the solutions into a four- to fivefold excess of ethanol. So obtained substances were filtered off and reprecipitated with ethanol after dissolution in  $50 \text{ cm}^3$  water. The products were washed with ethanol and ether, and dried over silica gel. The yields were 60 to 70%.

$[\text{CoH}_6(\text{mibmp})_2]$  and  $[\text{NiH}_6(\text{mibmp})_2] \cdot \text{H}_2\text{O}$ . A solution of 40 mmol  $\text{H}_4\text{mibmp}$  in  $50 \text{ cm}^3$  water was added to a suspension of 20 mmol of freshly precipitated and washed transition metal hydroxide in  $100 \text{ cm}^3$  water. The resulting solution was warmed, filtered, and transferred to about a fourfold excess of ethanol. The viscous precipitate formed was dissolved in  $50 \text{ cm}^3$  water, and transferred to a fourfold excess of ethanol. The finely crystalline product obtained was filtered off, washed with ethanol and ether, and dried over silica gel. The yields were about 50%.

$\text{M}[\text{CoH}(\text{mibmp})]_n \cdot \text{H}_2\text{O}$  ( $M = \text{Li}, \text{Na}, \text{K}$ ). 90 mmol of an alkali metal hydroxide and 30 mmol  $\text{H}_4\text{mibmp}$  were dissolved in 200 ml of a hot 1 : 1 methanol-water mixture, and 30 mmol  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$  was added to the solution. After cooling, ethanol was added, and the precipitate obtained was filtered off, dissolved in hot methanol, and on cooling reprecipitated with ethanol, filtered off, washed with acetone, and dried in air. Yields of about 80% were obtained.

$\text{Li}_5[\text{CoH}(\text{mibmp})_2] \cdot 9 \text{ H}_2\text{O}$ . 30 mmol LiOH and 30 mmol  $\text{H}_4\text{mibmp}$  were dissolved in 200 ml of a hot 1 : 1 methanol-water mixture, and 15 mmol  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$  was added to the solution. The product was isolated and recrystallized in the same way as described in the preceding paragraph.

$\text{Mg}_5[\text{Co}_2\text{H}_2(\text{mibmp})_4] \cdot 26 \text{ H}_2\text{O}$ ,  $\text{Ca}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 9 \cdot 5 \text{ H}_2\text{O}$ ,  $\text{Sr}_3[\text{Co}_2\text{H}_2(\text{mibmp})_3] \cdot 18 \text{ H}_2\text{O}$ , and  $\text{Ba}_4[\text{Co}_2(\text{mibmp})_3] \cdot 20 \text{ H}_2\text{O}$ . 12.3 mmol  $\text{H}_6\text{mibmp}$  and 15 mmol of the respective hydroxide (or hydroxide-carbonate in the case of magnesium) were dissolved in 100 ml water. After filtration, 5 mmol  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$  were dissolved in the solution. The finely crystalline product that precipitated on heating to  $70^\circ\text{C}$  was filtered off at the same temperature, washed with acetone, and dried in air. The compounds were obtained in yields of 20 to 30%.

$\text{M}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5]_n \cdot \text{H}_2\text{O}$  ( $M = \text{Mg(II)}, \text{Ca(II)}, \text{Sr(II)}$ ) and  $\text{Ba}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 7 \cdot 5 \text{ H}_2\text{O}$ . 30 mmol  $\text{H}_4\text{mibmp}$  and 45 mmol of the respective hydroxide (or hydroxide-carbonate in the case of magnesium) were dissolved in a hot 1 : 1 methanol-water mixture, and 15 mmol  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$  was added to the solution. The product obtained after cooling by precipitation with ethanol was filtered off, reprecipitated, washed with acetone, and dried in air. The yields ranged from 80 to 90%.

In the substances prepared, the alkali metals were determined by atomic absorption spectrophotometry, and the other metals were determined chelatometrically after sample combustion and dissolution of the residue in hydrochloric acid. Nitrogen was determined as  $\text{NH}_3$  by distillation on mineralization of the sample. The water was determined from the weight loss from 50 to  $200^\circ\text{C}$ . The analyses of the complexes are listed in Table I.

### Instruments

Infrared spectra were obtained on a Perkin-Elmer 225 instrument in the ranges  $400-4\,000\text{ cm}^{-1}$  in a Nujol mull and  $2\,000-4\,000\text{ cm}^{-1}$  in hexachlorobutadiene. The wavenumber scale of the instrument was calibrated with aid of a polystyrene foil. The magnetic susceptibility was measured at 298 K by the Faraday method, on a balance calibrated with cupric sulphate pentahydrate and sodium chloride. The diffusion reflectance spectra of the solid substances were obtained on a VSU-2 instrument (Zeiss, Jena) in the range  $200-1\,200\text{ nm}$ , using magnesium oxide as the reference substance. The electronic absorption spectra of aqueous solutions of the substances were measured with Unicam SP 800 and VSU-2 instruments, from 200 to 400 nm at a concentration of  $0.003\text{ mol dm}^{-3}$  and from 400 to 1 100 nm at concentrations between  $0.005$  and  $0.01\text{ mol dm}^{-3}$ , depending on the solubility of the substances studied, using 5 cm cells if necessary.

Orientative X-ray powder patterns were obtained by the Debye-Scherrer method on a Mikro-meta 2 instrument (Chirana).

## RESULTS AND DISCUSSION

### *Preparation of Complexes*

On the basis of the results of our study of the complexing properties of  $\text{H}_4\text{mibmp}$  in solution<sup>6</sup>, we attempted to prepare solid cobalt, nickel, copper and zinc complexes, both protonized and deprotonized, with metal-to-ligand ratios of 1 : 1 and 1 : 2. Protonized complexes of the type  $[\text{MH}_2(\text{mibmp})]$  were obtained for all the metals studied. The other complexes except  $[\text{CuH}_2(\text{mibmp})]\cdot\text{H}_2\text{O}$  could only be separated after precipitation with ethanol. The infrared spectra of all the compounds never showed any band due to ethanol ( $880-890\text{ cm}^{-1}$  and  $1\,300-1\,450\text{ cm}^{-1}$ ), and the character of the spectra corresponded to the respective hydrates. The spontaneously precipitated  $[\text{CuH}_2(\text{mibmp})]\cdot\text{H}_2\text{O}$  provided an X-ray powder pattern. Of the complexes that had been precipitated with ethanol, only  $[\text{ZnH}_2(\text{mibmp})]\cdot 2\text{H}_2\text{O}$  gave an X-ray powder pattern.

The 1 : 2 complexes, of the type  $[\text{MH}_6(\text{mibmp})_2]$ , could only be prepared with cobalt and nickel. An X-ray powder pattern was obtained only for  $[\text{CoH}_6(\text{mibmp})_2]$ . As in a previous work<sup>1</sup>, the effect of external ions on the precipitation and stoichiometry of solid cobalt complexes was investigated. Alkali metals formed solid complex salts with a molar metal-to-ligand ratio of 1 : 1 only, and these did not precipitate until ethanol was added to a methanolic solution. Attempts to prepare analogous 1 : 2 complexes were unsuccessful, except for  $\text{Li}_5[\text{CoH}(\text{mibmp})_2]\cdot 9\text{H}_2\text{O}$ . Because of these difficulties, we focused our attention on group II metals. Two methods of isolation the complex salts from solution were tested. Both of them started with a solution containing cobalt(II) chloride and the ligand in approximately the stoichiometric ratio, and the stoichiometric amount of a hydroxide with respect to  $\text{pH} \sim 7$ .

The first method, analogous to the preparation of alkali metal salts, consisted of precipitation with ethanol to give salts of the anion  $[\text{H}_6\text{Co}_2(\text{mibmp})_5]^{10-}$ , with the exception of barium, for which the complex  $\text{Ba}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 7.5 \text{H}_2\text{O}$  was isolated. Although the compounds of the above composition could be obtained in a reproducible way, they appeared as X-ray amorphous.

The other method, which consisted of heating an aqueous solution to 70–80°C, was successful in isolating the complexes  $\text{Mg}_5[\text{Co}_2\text{H}_2(\text{mibmp})_4] \cdot 26 \text{H}_2\text{O}$ ,  $\text{Ca}_2 \cdot [\text{CoH}_2(\text{mibmp})_2] \cdot 9.5 \text{H}_2\text{O}$ ,  $\text{Sr}_3[\text{Co}_2\text{H}_2(\text{mibmp})_3] \cdot 18 \text{H}_2\text{O}$ , and  $\text{Ba}_4[\text{Co}_2(\text{mibmp})_3] \cdot 20 \text{H}_2\text{O}$ . The products precipitated spontaneously and were isolated at the same temperature because they redissolved at room temperature. Orientative X-ray powder patterns were obtained for the four complexes.

Our experience with the preparation of the compounds is in accord with the well-known reluctance of aminoalkylphosphonic acid complexes to crystallize. Besides the large particle size, an important role is also played by hydration. Apparently, the substances are not able to crystallize until the hydration shell of the ion is dis-

TABLE I

Analytical and magnetic data. M = Li, Na, K, Mg, Ca, Sr, Ba

Compound	(Calculated) found				$\mu_{\text{eff}}$ B.M.
	% N	% Co, Ni, Cu, Zn	% M	% H <sub>2</sub> O	
$[\text{CoH}_2(\text{mibmp})] \cdot 3.5 \text{H}_2\text{O}$	(4.13) 4.14	(17.4) 17.5	—	(18.6) 18.6	4.99
$[\text{NiH}_2(\text{mibmp})] \cdot 3.5 \text{H}_2\text{O}$	(4.13) 4.15	(17.3) 17.4	—	(18.2) 18.1	3.07
$[\text{CuH}_2(\text{mibmp})] \cdot \text{H}_2\text{O}$	(4.69) 4.66	(21.3) 21.4	—	(6.4) 6.3	1.98
$[\text{ZnH}_2(\text{mibmp})] \cdot 2 \text{H}_2\text{O}$	(4.39) 4.35	(20.5) 20.6	—	(11.3) 11.2	—
$[\text{CoH}_6(\text{mibmp})_2]$	(5.66) 5.53	(11.8) 11.8	—	—	5.10
$[\text{NiH}_6(\text{mibmp})_2] \cdot \text{H}_2\text{O}$	(5.46) 5.43	(11.4) 11.5	—	(4.0) 4.1	3.05
$\text{Li}[\text{CoH}(\text{mibmp})] \cdot 4 \text{H}_2\text{O}$	(3.96) 3.93	(16.7) 16.6	(1.96) 1.99	(20.3) 20.6	5.10
$\text{Na}[\text{CoH}(\text{mibmp})] \cdot 3.5 \text{H}_2\text{O}$	(3.88) 3.84	(16.3) 16.2	(6.37) 6.30	(17.5) 17.5	4.92
$\text{K}[\text{CoH}(\text{mibmp})] \cdot 3 \text{H}_2\text{O}$	(4.67) 4.52	(19.6) 19.6	(13.0) 12.9	(18.0) 18.0	5.02
$\text{Li}_5[\text{CoH}(\text{mibmp})_2] \cdot 9 \text{H}_2\text{O}$	(4.09) 4.05	(8.58) 8.49	(5.05) 4.97	(23.6) 23.5	4.86
$\text{Mg}_5[\text{Co}_2\text{H}_2(\text{mibmp})_4] \cdot 26 \text{H}_2\text{O}$	(3.53) 3.42	(7.43) 7.37	(7.66) 7.56	(30.6) 29.4	5.21
$\text{Ca}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 9.5 \text{H}_2\text{O}$	(3.77) 3.65	(7.94) 7.78	(10.8) 10.4	(23.1) 22.5	5.41
$\text{Sr}_3[\text{Co}_2\text{H}_2(\text{mibmp})_3] \cdot 18 \text{H}_2\text{O}$	(8.71) 8.72	(3.10) 3.11	(19.4) 19.8	(24.0) 24.1	5.31
$\text{Ba}_4[\text{Co}_2(\text{mibmp})_3] \cdot 20 \text{H}_2\text{O}$	(2.51) 2.41	(7.05) 7.01	(32.8) 32.0	(21.5) 21.3	5.38
$\text{Mg}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 28 \text{H}_2\text{O}$	(3.84) 3.82	(6.46) 6.32	(6.66) 6.68	(27.6) 27.5	6.01
$\text{Ca}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 16 \text{H}_2\text{O}$	(4.15) 3.92	(6.98) 6.71	(11.9) 11.5	(17.1) 16.3	5.27
$\text{Sr}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 16 \text{H}_2\text{O}$	(3.65) 3.65	(6.14) 6.25	(22.8) 23.0	(15.0) 15.3	6.28
$\text{Ba}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 7.5 \text{H}_2\text{O}$	(3.10) 2.94	(6.53) 6.25	(30.4) 29.4	(15.0) 14.3	5.38

rupted, whether by alcohol addition or by heating. This is in agreement with the work of Samakayev and co-workers<sup>8</sup>, who studied the solubility of magnesium, calcium, strontium and barium salts of ethylenediaminetetramethylenephosphonic acid. The solubility of these compounds decreases with increasing temperature, a phenomenon which the authors explain as the result of the hydration energy being greater than the lattice energy.

### Spectral and Magnetic Properties

The dominant features of the infrared spectra of the compounds studied are bands in the region 900–1 200  $\text{cm}^{-1}$ . Their assignment is given in Table II. In agreement with the literature<sup>9–12</sup> and our previous results<sup>1</sup>, the bands are attributed to the coordination of oxygen atoms of the phosphonic groups. The calculated values of the effective magnetic moment (Table I) indicate that cobalt and nickel form high-spin complexes.

TABLE II  
Bands ( $\text{cm}^{-1}$ ) in the IR spectra in the region of the stretching vibrations of phosphonic group

Compound	$\nu_s \text{P(OH)}$	$\nu(\text{CN})$	$\nu_s(\text{PO}_2)$	$\nu_{\text{as}}(\text{PO}_2)$
$\text{H}_4\text{mibmp}$	933 959	1 004	1 030 1 071	1 111 1 163
$[\text{CoH}_6(\text{mibmp})_2]$	930	1 000	1 030 1 075	1 140 1 155 1 180 1 190
$[\text{NiH}_6(\text{mibmp})_2] \cdot \text{H}_2\text{O}$	934	1 000	1 033 1 085	1 149 1 160 1 189
	$\nu_s(\text{PO}_3)$			$\nu_{\text{as}}(\text{PO}_3)$
$\text{Li}[\text{CoH}(\text{mibmp})] \cdot 4 \text{H}_2\text{O}$	940	995	1 060 1 140	
$\text{Na}[\text{CoH}(\text{mibmp})] \cdot 3 \cdot 5 \text{H}_2\text{O}$	935	990	1 045 1 140	
$\text{K}[\text{CoH}(\text{mibmp})] \cdot 3 \text{H}_2\text{O}$	930	990	1 065 1 130	
$\text{Li}_5[\text{CoH}(\text{mibmp})_2] \cdot 9 \text{H}_2\text{O}$	945 975	995	1 075 1 140	
$\text{Mg}_5[\text{Co}_2\text{H}_2(\text{mibmp})_4] \cdot 26 \text{H}_2\text{O}$	975	995	1 080 1 100	
$\text{Ca}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 9 \cdot 5 \text{H}_2\text{O}$	935	995	1 080 1 115	
$\text{Sr}_3[\text{Co}_2\text{H}_2(\text{mibmp})_3] \cdot 18 \text{H}_2\text{O}$	940 975	995	1 080 1 105	
$\text{Ba}_4[\text{Co}_2(\text{mibmp})_3] \cdot 20 \text{H}_2\text{O}$	970	985	1 090sb	
$\text{Mg}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 28 \text{H}_2\text{O}$	975	990	1 080 1 105	
$\text{Ca}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 16 \text{H}_2\text{O}$	915 980	1 000	1 055 1 090	1 125 1 170 1 195
$\text{Sr}_5[\text{Co}_2\text{H}_6(\text{mibmp})_5] \cdot 16 \text{H}_2\text{O}$	945 965	995	1 030 1 080	1 100 1 155 1 170 1 195
$\text{Ba}_2[\text{CoH}_2(\text{mibmp})_2] \cdot 7 \cdot 5 \text{H}_2\text{O}$	930 970	990		1 100sb
$[\text{CoH}_2(\text{mibmp})] \cdot 3 \cdot 5 \text{H}_2\text{O}$	930 970	990	1 075 1 130	1 175
$[\text{NiH}_2(\text{mibmp})] \cdot 3 \cdot 5 \text{H}_2\text{O}$	932	995	1 075 1 100	1 123 1 144
$[\text{CuH}_2(\text{mibmp})] \cdot \text{H}_2\text{O}$	940 966	1 007	1 036 1 059	1 148 1 162 1 183
$[\text{ZnH}_2(\text{mibmp})] \cdot 2 \text{H}_2\text{O}$	939 977	1 015	1 030 1 084	1 088 1 128 1 181

TABLE III  
Ligand-field spectral data

Compound	Reflectance (transmittance) · 10 <sup>-3</sup> , cm <sup>-1</sup>
[NiH <sub>2</sub> (mibmp)].3.5 H <sub>2</sub> O	24.4 (25.0)
[NiH <sub>6</sub> (mibmp) <sub>2</sub> ].H <sub>2</sub> O	24.4 (25.0)
[CuH <sub>2</sub> (mibmp)].H <sub>2</sub> O	14.7 (14.7)
[CoH <sub>2</sub> (mibmp)].3.5 H <sub>2</sub> O	13.9 (14.3)
[CoH <sub>6</sub> (mibmp) <sub>2</sub> ]	13.2 (13.5)
M[CoH(mibmp)].nH <sub>2</sub> O <sup>a</sup>	14.3—11.8 (14.3—11.8)
Li <sub>3</sub> [CoH(mibmp) <sub>2</sub> ].9 H <sub>2</sub> O	18.7 (19.2)
Mg <sub>5</sub> [Co <sub>2</sub> H <sub>2</sub> (mibmp) <sub>4</sub> ].26 H <sub>2</sub> O	18.9 (19.4)
Ca <sub>2</sub> [CoH <sub>2</sub> (mibmp) <sub>2</sub> ].9.5 H <sub>2</sub> O	18.5 (19.1)
Sr <sub>3</sub> [Co <sub>2</sub> H <sub>2</sub> (mibmp) <sub>3</sub> ].18 H <sub>2</sub> O	18.5 (19.0)
Ba <sub>4</sub> [Co <sub>2</sub> (mibmp) <sub>3</sub> ].20 H <sub>2</sub> O	18.5 (18.8)
Mg <sub>5</sub> [Co <sub>2</sub> H <sub>6</sub> (mibmp) <sub>5</sub> ].28 H <sub>2</sub> O	18.5 (18.8)
Ca <sub>5</sub> [Co <sub>2</sub> H <sub>6</sub> (mibmp) <sub>5</sub> ].16 H <sub>2</sub> O	18.5 (19.0)
Sr <sub>5</sub> [Co <sub>2</sub> H <sub>6</sub> (mibmp) <sub>5</sub> ].16 H <sub>2</sub> O	18.9 (19.1)
Ba <sub>2</sub> [CoH <sub>2</sub> (mibmp) <sub>2</sub> ].7.5 H <sub>2</sub> O	18.5 (18.9)
	20.8 sh (21.5) sh
	20.8 sh (21.5) sh
	(20.5) sh
	20.0 sh (20.6) sh
	20.0 sh (20.0) sh
	20.0 sh (21.3, 20.4)
	20.0 sh (20.0) sh
	20.0 sh (21.0 sh, 20.0) sh
	20.0 sh (20.1) sh
	(20.5) sh
	20.4 sh (20.6)
	20.0 sh (20.0) sh
	13.0 (13.3)
	8.3 (8.3)
	13.2 (13.5)
	17.2 sh
	17.2 sh
	17.2
	17.2
	17.2 (17.2)
	17.4
	17.5
	17.5 sh
	17.2
	17.2—15.9
	17.2 sh
	17.2 sh

<sup>a</sup> M = Li, Na, K.

The electronic absorption spectra of the copper complexes are in very good agreement with the diffusion reflectance spectra. A broad absorption band is observed, which arises from the transition  $\nu_1(^2T_{2g} \leftarrow ^2E_g)$  with assumed coordination number of six (Table III). For the nickel complexes, the two kinds of spectra agree sufficiently (see Table III). The band positions correspond to a coordination number of six. The  $\nu_1$  band positions for the two complexes give the values of  $10Dq$ . The calculated value of  $f_L$  for  $H_4mibmp$  lies between 0.82 and 0.86 for the copper complexes and between 0.91 and 0.95 for the nickel complexes. The values of  $g_C$  were taken from the literature<sup>13,14</sup>. The value for the copper complexes is not, however, very precise because of the well-known width of the  $\nu_1$  band.

Comparison of the calculated Jorgenson parameter  $f_L$  for  $H_4mibmp$  with values tabulated for other ligands<sup>14</sup> shows that it is close to that of water. The value of  $f_L$  for Ni complexes with  $H_4mibmp$  is somewhat lower than that for Ni complexes with  $H_6ntmp$  (ref.<sup>1</sup>), as a result of fewer phosphonic groups in the molecule and hence a lower chelating ability. The electronic absorption spectra of the cobalt complexes show an absorption band at about 525 nm, which is characteristic of cobalt compounds with octahedral coordination. In the case of the diffusion reflectance spectra, the band at 525 nm shifts and new shoulders or weak bands appear (Table III). This phenomenon probably corresponds to a tetragonal distortion in the solid state. The spectra for the other complexes exhibited three bands in the visible region (Table III), which apparently are also associated with the tetragonal sphere of cobalt<sup>13</sup>.

Intense absorption bands in the ultraviolet region were observed for the copper, nickel and cobalt complexes: copper complexes gave bands in the regions 215 to 220 nm and 270–280 nm, nickel complexes in the region 210–220 nm, and cobalt complexes in the region 215–230 nm. Since no corresponding intense bands were found in the absorption spectrum of the ligand itself, these bands apparently arise from charge transfer.

The results obtained indicate that, as in the case of the analogous  $H_6ntmp$  complexes<sup>1</sup>, the central atoms in the complexes studied here have an octahedral or tetrahedral environment consisting of oxygen atoms. An exception is the copper complexes, where coordination by the nitrogen atom cannot be excluded in view of the high stability constant<sup>6</sup>.

#### REFERENCES

1. Lukeš I., Rejšková D., Odvárko R., Vojtišek P.: *Polyhedron* 5, 2063 (1986).
2. Pata N., Rao B. V., Dubey S. N., Puri D. M.: *Polyhedron* 3, 527 (1984).
3. Appleton G., Hall J. R., McMahon J.: *Inorg. Chem.* 25, 720 (1986).
4. Cummins D., van Soet T. C., Roijers E.: *Proceedings of The XXI International Conference on Coordination Chemistry, Toulouse 1980*; p. 366.
5. Głowiak T., Sawka-Dobrowolska W., Jezowska-Treibiatovska B., Antonow A.: *J. Cryst. Mol. Struct.* 10, 1 (1980).

6. Lukeš I., Dominák I.: Chem. Papers, in press.
7. Moedritzer K., Irani R. R.: J. Org. Chem. *31*, 1603 (1966).
8. Samakaev R. Kh., Dyatlova N. M., Dytyuk L. T., Yaroshenko G. F.: Zh. Neorg. Khim. *29*, 2931 (1984).
9. Nakamoto K., Morimoto J., Martell A. E.: J. Am. Chem. Soc. *85*, 309 (1963).
10. Nakamoto K.: *Infrared Spectra of Inorganic and Coordination Compounds*, pp. 117, 239. Wiley, New York 1970.
11. Nakamoto K., McCarthy P. J.: *Spectroscopy and Structure of Metal Chelate Compounds*, p. 187. Wiley, New York 1968.
12. Nikitina L. V., Grigoreyev A. I., Dyatlova N. M.: Zh. Obshch. Khim. *44*, 1598 (1974).
13. Lever A. B.: *Inorganic Electronic Spectroscopy*, p. 491. Elsevier, Amsterdam 1984.
14. Jorgenson C. K.: *Absorption Spectra and Chemical Bonding in Complexes*, p. 122. Pergamon Press, Oxford 1962.

Translated by M. Škubalová.