

## THE COMPLEXES OF IMINODIACETIC ACID WITH DIVALENT MANGANESE AND IRON

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*Dedicated to Professor Dr S. Škramovský on the occasion of his 80th birthday.*

Complexes of the type  $M_2[Me(IDA)_2]$  and  $MeIDA \cdot nH_2O$ , where  $M = H^+, Li^+, Na^+, K^+, 1/2 Ba^{2+}$ ,  $Me = Mn^{2+}, Fe^{2+}$  and  $IDA = [NH(CH_2COO)_2]^{2-}$  were prepared in the solid state. The magnetic properties, thermal stability and electron and infrared spectra of these substances were studied. It followed from the results that both prepared types of complex have a high spin octahedral configuration. In contrast to  $M_2[Me(IDA)_2]$  type complexes, complexes of the  $MeIDA \cdot nH_2O$  type have polymeric character.

The anions of iminodiacetic acid  $IDA = [NH(CH_2COO)_2]^{2-}$  belong among tridentate ligands which can be coordinated to the central atom through two carboxyl groups and a nitrogen atom. Iminodiacetic acid forms complexes with molar ratios, metal : ligand, of 1 : 1 and 1 : 2 with the transition metals. Complexes with molar ratios of 1 : 2 can exist in three isomeric forms, of which one has the nitrogen atom in the *cis* position and two have the nitrogen atom in the *trans* position (facial and meridional). This isomerism has been studied for cobalt(III) complexes<sup>1</sup>, where, of the two possible *trans* arrangements, the authors favour the facial arrangement, which is preferable because of the bonding angles of the ligands. Complexes with Mn(II) and Fe(II) in a 1 : 2 ratio have been studied practically only in solution<sup>2,3</sup>, where they are less stable than the complexes of the other divalent transition metals<sup>3</sup>. Only the dihydrate of manganese(II)bis(iminodiacetic) acid,  $H_2Mn(IDA)_2 \cdot 2H_2O$ , has been prepared in the solid state<sup>4</sup>. Complexes with molar ratios of 1 : 1 have not yet been studied in the solid state.

### EXPERIMENTAL

#### Reagents and Apparatus

Iminodiacetic acid was the product of BDH Chemicals Ltd, England, and the other chemicals were the products of Lachema, Czechoslovakia. The thermal stabilities of the complexes were studied by following the mass loss of the substance in a drying box in which the temperature

increased by about 10°C in 8 h. The powder diagrams of the substances thermally decomposed at 500°C were measured by the Debye-Scherrer method on a Mikrometa 2 instrument from the firm Chirana, Czechoslovakia. The magnetic measurements were carried out at 298 K by the Faraday method and diamagnetic correction was made using Pascal constants<sup>5</sup>. The ligand diamagnetism was found experimentally ( $58 \cdot 10^{-6}$ ). Infrared spectra were measured in KBr and triphenyl suspensions on a UR 20 instrument from the firm Zeiss, Jena. Electronic spectra of aqueous solutions were measured on Unicam SP 800 and VSU-2 (Zeiss, Jena, GDR) instruments.

#### Preparation of Complexes with Ratio Me : IDA = 1 : 1, where Me = Mn or Fe

Manganese iminodiacetate, MnIDA.6 H<sub>2</sub>O, and ferrous imino diacetate, FeIDA.2 H<sub>2</sub>O, were prepared by reaction of 2M solutions of manganese(II) and ferrous chlorides neutralized by a stoichiometric amount of iminodiacetate under nitrogen atmosphere. The solutions were heated to the boiling point on a water bath and evaporated to about half the original volume. After cooling with a water-ice mixture, pink crystals of manganese(II) iminodiacetate or white crystals of ferrous iminodiacetate were formed, which were filtered off in the air and washed with ethanol and ether. The yields of the reactions were 70% for manganese(II) iminodiacetate and 27% for ferrous iminodiacetate.

#### Preparation of Complexes with Ratio Me : IDA = 1 : 2

a) Preparation of bis(iminodiacetato)manganous acid. Iminodiacetic acid, manganese(II) chloride and potassium hydroxide were dissolved step-wise in water in the air in stoichiometric amounts (2 : 1 : 2). The solution was heated to the boiling point; on cooling, white crystals were formed, which were filtered off, washed with water, ethanol and ether and dried in the air. The reaction yield is 71%.

b) Preparation of lithium, sodium potassium and barium(II) salts of bis(iminoacetato)manganous acid. In each case, a 1–2M solution of the corresponding alkali iminoacetate with 10% excess iminodiacetic acid over the stoichiometric amount were added to 0.03 mol of solid MnIDA.6 H<sub>2</sub>O. The solution was evaporated on a water bath to about one third and was left to crystallize in a nitrogen atmosphere. The precipitated white crystals were filtered off in the air, washed with ethanol and ether and dried over NaOH in a nitrogen atmosphere. The reaction yield is 55–59% with respect to iminodiacetic acid.

c) Preparation of the lithium, sodium and potassium salts of bis(iminodiacetato)ferrous acid. An amount of 50 ml of 1M ferrous chloride solution whose pH was adjusted with a 2% solution of the corresponding alkali hydroxide to a value of 2–3 under a nitrogen atmosphere was mixed with a 1M solution of the iminodiacetate of the alkali metal containing a 10% excess of iminodiacetic acid over the stoichiometric amount. The solution was evaporated on a water bath to about one half. The light yellow complex crystallized from hot solution and was rapidly filtered off and washed with an ice-cold mixture of 1 : 1 water-ethanol and then with ethanol and ether. The substances were dried over NaOH in a nitrogen atmosphere. The yield of the reaction was 13–16%.

## RESULTS AND DISCUSSION

All the complexes except bis(iminodiacetato)manganous acid had to be prepared in an inert atmosphere. In every case a 10% excess of iminodiacetic acid was added over the stoichiometric amount<sup>6</sup>. Thus the pH value was simultaneously shifted

to pH 5–6 at which the high sensitivity to atmospheric oxygen is decreased compared to highly alkaline solutions. The salts of bis(iminodiacetato)manganous acid cannot be prepared directly from manganese(II) chloride because of the similar solubility of the alkali chloride and the complex formed. The solid substances are not oxidized in the air. The compositions of the individual prepared complexes and their analyses are given in Table I.

Table II gives the course of the thermal decomposition of the prepared complexes. It followed from the study that, on prolonged standing, manganese(II) iminodiacetate is dehydrated to the 3·5 hydrate. The dehydration of the salts of manganese(II) bis(iminodiacetate) proceeds in one to two steps; dehydration of all salts is complete at 160°C. Bis(iminodiacetato)manganous acid was prepared in the anhydrous state, in contrast to the literature<sup>4</sup>. No region was found in which the anhydrous ferrous imino diacetate and the anhydrous salts of bis(iminodiacetato)ferrous acid would be stable in the air and dehydration occurred simultaneously with decomposition of the complex. Powder X-ray patterns of the products of decomposition of the complexes with molar ratios of 1 : 1 indicate that the product of the decomposition is always the corresponding oxide, *i.e.* the nonstoichiometric manganese oxide  $MnO_{1-2}$  and ferrous-ferric oxide  $Fe_3O_4$ . In addition to the diffraction lines corresponding to the transition metal oxide, the X-ray patterns of the product of thermal decomposition of the complexes also contained diffraction lines corresponding to the carbonates for sodium and potassium salts, the peroxide for the barium(II) salt and the oxide for the lithium salt.

TABLE I  
Results of analysis of the prepared complexes

Complex	Found/Calculated							
	% M		% Me		% N		% H <sub>2</sub> O	
Mn IDA.6 H <sub>2</sub> O	—	—	18.65	(18.69)	4.89	(4.76)	46.4	(36.7)
H <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	—	—	17.14	(17.24)	8.61	(8.78)	—	—
Li <sub>2</sub> [Mn(IDA) <sub>2</sub> ].4 H <sub>2</sub> O	3.40	(3.44)	13.86	(13.64)	7.07	(6.96)	18.0	(17.0)
Na <sub>2</sub> [Mn(IDA) <sub>2</sub> ].7.5 H <sub>2</sub> O	9.11	(9.23)	10.97	(11.03)	5.69	(5.62)	27.0	(27.2)
K <sub>2</sub> [Mn(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	6.50	(6.49)	12.82	(12.74)	6.50	(6.49)	8.3	(8.4)
Ba[Mn(IDA) <sub>2</sub> ].5 H <sub>2</sub> O	24.90	(25.24)	10.08	(10.10)	5.16	(5.14)	16.3	(16.6)
Fe IDA.2 H <sub>2</sub> O	—	—	25.11	(15.05)	6.21	(6.28)	16.7	(16.2)
Li <sub>2</sub> [Fe(IDA) <sub>2</sub> ].3 H <sub>2</sub> O	3.67	(3.60)	14.42	(14.43)	7.21	(7.25)	14.4	(14.0)
Na <sub>2</sub> [Fe(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	11.53	(11.49)	13.96	(13.96)	6.89	(7.00)	0.1	(9.0)
K <sub>2</sub> [Fe(IDA) <sub>2</sub> ].0.5 H <sub>2</sub> O	19.18	(19.26)	13.75	(13.35)	6.81	(6.90)	3.0	(2.2)

The determined values of the effective magnetic moment of the prepared substances are listed in Table III. The values for the iron complex are in good agreement with the values published<sup>5</sup> for the Fe(II) complex. For the manganese complex, the values of the effective magnetic moment are lower but always lie in the range

TABLE II

Thermal decomposition of the complexes

Compound	Temperature range, °C	Characteristics of the process
Mn IDA.6 H <sub>2</sub> O	0—20	—2.5 H <sub>2</sub> O
Mn IDA.3.5 H <sub>2</sub> O	100—140	—2.0 H <sub>2</sub> O
Mn IDA. 1.5 H <sub>2</sub> O	160—180	—1.5 H <sub>2</sub> O
Mn IDA	190—210	decomposition
H <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	150—220	decomposition
Li <sub>2</sub> [Mn(IDA) <sub>2</sub> ].4 H <sub>2</sub> O	30—120	—4.0 H <sub>2</sub> O
Li <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	170—200	decomposition
Na <sub>2</sub> [Mn(IDA) <sub>2</sub> ].7.5 H <sub>2</sub> O	30—80	—6.0 H <sub>2</sub> O
Na <sub>2</sub> [Mn(IDA) <sub>2</sub> ].1.5 H <sub>2</sub> O	100—120	—1.5 H <sub>2</sub> O
Na <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	170—240	decomposition
K <sub>2</sub> [Mn(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	30—120	—2.0 H <sub>2</sub> O
K <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	160—200	decomposition
Ba[Mn(IDA) <sub>2</sub> ].5 H <sub>2</sub> O	20—110	—4.0 H <sub>2</sub> O
Ba[Mn(IDA) <sub>2</sub> ].H <sub>2</sub> O	150—160	—1.0 H <sub>2</sub> O
Ba[Mn(IDA) <sub>2</sub> ]	170—210	decomposition
Fe IDA.2 H <sub>2</sub> O	140—180	—2.0 H <sub>2</sub> O
Fe IDA	180—240	decomposition
Li <sub>2</sub> [Fe(IDA) <sub>2</sub> ].3 H <sub>2</sub> O	100—160	—3.0 H <sub>2</sub> O
Li <sub>2</sub> [Fe(IDA) <sub>2</sub> ]	160—200	decomposition
Na <sub>2</sub> [Fe(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	100—160	—2.0 H <sub>2</sub> O
Na <sub>2</sub> [Fe(IDA) <sub>2</sub> ]	160—200	decomposition
K <sub>2</sub> [Fe(IDA) <sub>2</sub> ].0.5 H <sub>2</sub> O	100—140	—0.5 H <sub>2</sub> O
K <sub>2</sub> [Fe(IDA) <sub>2</sub> ]	160—220	decomposition

already observed for this type of substance. It follows from the determined values of the effective magnetic moment that all the complexes have high spin.

The study of the infrared spectra was concerned with the vibrational absorption bands, which are directly connected with coordination of the nitrogen and oxygen atoms to the central atom, *i.e.* vibrations of the N—H, C—N and —COO<sup>-</sup> groups. The values of the frequencies of the bands of these vibrations are listed in Table III. The shift in the absorption band of the valence vibration of the N—H group to lower wavenumbers can be used to detect the coordination of the nitrogen atom to the central atom<sup>7,8</sup>. This shift is also affected by the hydrogen bond of the N—H group with the water molecule in the crystallohydrates. The absorption band of the valence vibration of the N—H group may coincide with the absorption band for the valence vibration of OH(H<sub>2</sub>O). Consequently, for the Mn(II) salt, the spectra of the complexes partially dehydrated at 120°C were also measured. A shift of an average of 50 cm<sup>-1</sup> for all the studied complexes except H<sub>2</sub>[(IDA)<sub>2</sub>] compared to the frequency of 3 330 cm<sup>-1</sup> for sodium iminodiacetate indicate coordination of the nitrogen atom to the central atom. Bis-(iminodiacetato)manganous acid differs from the other complexes in having a value of 3 080 cm<sup>-1</sup>. A number of authors<sup>9-11</sup> have stated that valence vibrations of the C—N group of about 1 000 to 1 100 cm<sup>-1</sup>, shifted to lower values, indicate coordination of the nitrogen atom to the central atom. The spectra of the studied compounds contain bands shifted to 1 000 cm<sup>-1</sup>, but

TABLE III  
Infrared spectra and magnetic properties of the complexes

Complex	$\nu(\text{N—H})$ cm <sup>-1</sup>	$\nu(\text{N—H})$ cm <sup>-1</sup> dehydr.	$\nu_s(\text{CO}_2)$ cm <sup>-1</sup>	$\nu_{as}(\text{CO}_2)$ cm <sup>-1</sup>	$\mu_{\text{ef}}$ B.M.
Mn IDA.6 H <sub>2</sub> O	3 330 s	3 290 s	1 410 s	1 590 vs	5.56
H <sub>2</sub> [Mn(IDA) <sub>2</sub> ]	3 080 m	—	1 410 s	1 590 vs	5.74
Li <sub>2</sub> [Mn(IDA) <sub>2</sub> ].4 H <sub>2</sub> O	3 270 b, s	3 280 vs	1 405 vs	1 615 vs	5.56
Na <sub>2</sub> [Mn(IDA) <sub>2</sub> ].7.5 H <sub>2</sub> O	3 200 m	3 300 s	1 410 vs	1 620 vs	5.95
	3 235—80 b	3 325 vs			
K <sub>2</sub> [Mn(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	3 260 vs	3 250 vs	1 395 vs	1 600 vs	5.75
Ba[Mn(IDA) <sub>2</sub> ].5 H <sub>2</sub> O	3 240— —3 270 s, b	3 290 vs	1 410 s	1 600 vs	5.66
Fe IDA. 2H <sub>2</sub> O	3 300 m	—	1 405 s	1 585 vs	5.36
Li <sub>2</sub> [Fe(IDA) <sub>2</sub> ].3 H <sub>2</sub> O	3 290 s	—	1 410 vs	1 600 vs	5.40
Na <sub>2</sub> [Fe(IDA) <sub>2</sub> ].2 H <sub>2</sub> O	3 290 s	—	1 415 vs	1 620 vs	5.43
K <sub>2</sub> [Fe(IDA) <sub>2</sub> ].0.5 H <sub>2</sub> O	3 300 s	—	1 415 vs	1 600 vs	5.34

this region is so complicated that unambiguous conclusions cannot be drawn. The absorption bands of the symmetric valence vibration of the  $\text{—COO}^-$  group for all the prepared compounds lie in the narrow interval  $1\,395\text{—}1\,415\text{ cm}^{-1}$ . The bands of the antisymmetric valence vibration of the  $\text{COO}^-$  group for the complexes with a molar ratio of 1 : 1 and for bis(iminodiacetato)manganous acid lie in the range  $1\,585\text{—}1\,590\text{ cm}^{-1}$ . The difference between the frequencies of the absorption bands of the symmetric and antisymmetric valence vibrations,  $\Delta$ , is in the range  $170$  to  $185\text{ cm}^{-1}$ , indicating bidentate coordination of the carboxyl group<sup>12</sup>. The bands of the antisymmetric valence vibration of the  $\text{—COO}^-$  group for complexes with molar ratios of 1 : 2 lie in the region  $1\,600\text{—}1\,620\text{ cm}^{-1}$  and the difference  $\Delta \approx 210\text{ cm}^{-1}$ , indicating monodentate coordination of the carboxyl group.

No absorption maximum was found in the electronic spectra of the Mn(II) complexes. The electronic spectra of the Fe(II) complexes contained an absorption band in the region  $950\text{—}1\,100\text{ nm}$ . This band is broad and partially split and corresponds to the transition from the  ${}^5T_{2g}$  state to the  ${}^5E_g$  state.

Dehydration of the last water molecules in the region  $150\text{—}180^\circ\text{C}$  for MnIDA.  $.6\text{ H}_2\text{O}$  and FeIDA.  $2\text{ H}_2\text{O}$ , the bidentally coordinated carboxyl group and the observed low solubility<sup>6</sup> indicate the same structural model as that for the dihydrate of copper(II) iminodiacetate<sup>13</sup>. The central atom is coordinated to the two water molecules and to iminodiacetic acid through the nitrogen atom of the NH group and the oxygen atoms of the carboxyl groups. The bidentate bonds of iminodiacetic acid lead to connection of the octahedra with polymer formation. The structure of bis(iminodiacetato)manganous acid apparently corresponds to this structure. The shift of the absorption band of the valence vibration of the NH group to a value of  $3\,080\text{ cm}^{-1}$  and the absence of a band for the antisymmetric valence vibration of the  $\text{—COOH}$  group in the region  $1\,700\text{—}1\,800\text{ cm}^{-1}$  corresponds to formation of the protonated  $\text{—NH}_2^+$  group rather than to metal coordination. The manganese atom would then be surrounded by six oxygen atoms from the carboxyl groups, of which one carboxyl group of iminodiacetic acid is always bonded bidentally. Isolated octahedra are formed with the complexes with molar ratios of 1 : 2, where two iminodiacetic acid molecules are coordinated to the central atom. Of the possible ligand arrangements, most probably the isomer with the nitrogen atoms in the *trans* position will be formed. The intensity and character of the bands in the electronic spectra of the iron complexes<sup>12</sup> correspond to this isomer. The bonding angles in iminodiacetic acid<sup>14</sup> and in the determined structures<sup>14,15</sup> indicate that *trans*-facial isomerism is involved.

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