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A Study of Bis(iminodiacetato)cobaltates(II) and (III)

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Compounds of the type cis-*$M[Co(ida)_2]\cdot nH_2O$ and* trans-*$M[Co(ida)_2]\cdot nH_2O$ and $M_2[Co(ida)_2]\cdot nH_2O$, where $M = H^+$, Li^+, Na^+, K^+, $\frac{1}{2}Ba^{2+}$ and ida = $NH(CH_2COO^-)_2$, were prepared. The infrared and electronic spectra of these compounds and the redox potential of the Co^{2+}/Co^{3+} couple were studied. The results obtained indicate an octahedral configuration of the ligands around cobalt. During the preparation of the complexes of the $M_2[Co(ida)_2]$ type, oxidation of Co(II) and formation of the $M[Co(ida)_2]$ complexes were observed. The content of the Co(III) depends on the alkali metal present and increases in the order, Li^+, Na^+, K^+, Rb^+, Cs^+.*

Introduction

In the study of the complexes of iminodiacetic acid (H_2ida) with cobalt, attention has chiefly been centered on the complexes with Co(III). Both possible geometric isomers with the *cis* and *trans* arrangement of the nitrogen atoms, *cis*-$K[Co(ida)_2]\cdot 2.5H_2O$ and *trans*-$K[Co(ida)_2]\cdot 2H_2O$, have been prepared [1, 2]. Among the possible arrangements of iminodiacetic acid and the *trans* isomers, a *trans*-facial arrangement is assumed in view of the bond angles in iminodiacetic acid alone. The structure of *cis*-$K[Co(ida)_2]\cdot 2.5H_2O$ has been found by X-ray measurements [3]. Cook [4] prepared the corresponding acids, *cis*-$H[Co(ida)_2]$ and *trans*-$H[Co(ida)_2]\cdot 4H_2O$. The iminodiacetic acid complexes with Co(II) with a ratio of 2:1 were mostly studied in solution [5]. The only compound, $Na_2[Co(ida)_2]\cdot 8H_2O$, was prepared in the solid state by Laitinen [6] and its thermal decomposition and reflectance spectra were studied.

Experimental

The infrared spectra were recorded on a UR-20 instrument (Zeiss, Jena) within a region of 400 to 4000 cm^{-1} in KBr pellets, from 400 to 1800 cm^{-1} in nujol mull and from 1800 to 3800 cm^{-1} in tripene. The spectra of the partially dehydrated compounds were also measured in tripene at 100 °C.

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 measured on a VSU-2 instrument (Zeiss, Jena), using magnesium oxide as reference, from 200 to 1100 nm. The absorption electronic spectra of aqueous solutions were obtained with the VSU-2 instrument from 200 to 250 nm at a concentration of 8×10^{-4} *M*, from 250 to 300 nm at a concentratin of 4×10^{-3} *M* and from 300 to 1000 nm at a concentration of 0.1 *M*.

The stability of aqueous solutions of the $[Co(ida)_2]^{2-}$ complexes was studied by measuring the electronic absorption spectra from 300 to 700 nm on a Unicam SP 800 instrument. Solutions with concentrations of 0.5–0.1 *M* were prepared by dissolving the complexes in water, other solutions were prepared in the following manner: 2×10^{-3} mol H_2ida were dissolved in 10 ml H_2O, adding 2×10^{-3} mol M_2CO_3 (M = Li, Na, K, Rb, Cs) and 10^{-3} mol $CoCl_2\cdot 6H_2O$. This solution was allowed to stand in the air at laboratory temperature. After 2 days the mixture of partially evaporated solution and the solid phase precipitated was transferred to a volumetric flask and diluted with water to 10 ml. The 0.1 *M* solution obtained was measured in a 10 mm cuvette against water.

The redox potential of the $[Co(ida)_2]^{2-}/[Co(ida)_2]^-$ system was measured in a solution containing 0.1 *M* $Na_2[Co(ida)_2]$ and $Na[Co(ida)_2]$ whose pH was adjusted to *ca.* 2 by hydrochloric acid, controlling the pH during the measurement by adding 1 *M* NaOH. A PHM 64 pH-meter (Radiometer) was used, measuring the pH with a GK 2303 C combined electrode and the potential with a P 101 platinum and a K 401 calomel electrode. The redox potential of this system was further checked by measuring the half-wave potential of $M[Co(ida)_2]^-$, using an LP-7c polarograph (Laboratorní prístroje, Prague), against an AgCl/Ag electrode in a 0.1 *M* LiCl solution. The complex studied was dissolved either in a 0.1 *M* $LiClO_4$ solution (the $Li[Co(ida)_2]$ salt), or in the appropriate nitrate (with $Na[Co(ida)_2]$ and $K[Co(ida)_2]$ salts).

In the substances prepared, the alkali metals were determined by atomic absorption spectrometry, cobalt chelatometrically after sample combustion and dissolution of the residue in hydrochloric acid and nitrogen by distillation as NH_3 after sample mineralization.

Co(II) in the presence of Co(III) was determined by potentiometric titration with $Ce(SO_4)_2$ with addition of EDTA. Water was determined from the weight loss during stationary drying from 50 to 200 °C. Iminodiacetic acid was obtained from SAS Scientific Chemicals Ltd. and the other chemicals were products of Lachema, Czechoslovakia.

Preparations

$Li_2[Co(ida)_2]\cdot 6H_2O$, $Na_2[Co(ida)_2]\cdot 7H_2O$ and $Ba[Co(ida)_2\cdot 8H_2O$ were prepared by dissolving 0.05 mol iminodiacetic acid, the stoichiometric amount of the appropriate hydroxide and 0.02 mol $CoCl_2\cdot 6H_2O$ in 200–150 ml water. The solution volume was evaporated to one half and after cooling the crystalline product was separated, washed with ethanol and ether. The yield was 50–65%. $Na_2[Co(ida)_2]\cdot 8H_2O$ was further prepared according to Laitinen [6] by dissolving cobalt(II) carbonate in a solution of iminodiacetic acid and neutralizing the solution.

$H_2[Co(ida)_2]$ and $K_2[Co(ida)_2]\cdot 4H_2O$ were prepared by conversion of $Ba[Co(ida)_2]$ with sulphuric acid and potassium sulphate respectively in the stoichiometric ratio. After filtering off the $BaSO_4$, the solution of the potassium salt was allowed to crystallize over P_2O_5 in an N_2 atmosphere and that of $H_2[Co(ida)_2]$ was precipitated with ethanol. Both products were isolated in the same way as above. The yields were 39% for $K_2[Co(ida)_2]\cdot 4H_2O$ and 72% for $H_2[Co(ida)_2]$. *Cis*-$Na[Co(ida)_2]\cdot 2H_2O$ and *cis*-$K[Co(ida)_2]\cdot 2.5H_2O$ were prepared by dissolving 0.053 mol iminodiacetic acid, 0.1 mol of the appropriate hydroxide and 0.021 mol $CoCl_2\cdot 6H_2O$ in 40 ml H_2O, followed by oxidation with 7 ml 30% H_2O_2 at 0 °C. The product separated was filtered off after several hours and washed with ethanol and ether. The average yield was 60%.

Trans-$K[Co(ida)_2]\cdot 2H_2O$ was prepared by dissolving 0.053 mol iminodiacetic acid, 0.11 mol KOH and 0.017 mol $CoCl_2\cdot 6H_2O$ in 40 ml H_2O, followed by oxidation with 1 ml 30% H_2O_2 at 80 °C. After ½ hour the solution was cooled to 15 °C, the product was filtered off, recrystallized from hot water and washed with ethanol and ether. The yield amounted to 64%.

Cis-$Ba[Co(ida)_2]_2\cdot 4.5H_2O$ and *trans*-$Ba[Co(ida)_2]_2\cdot 5.5H_2O$ were prepared by dissolving 0.041 mol iminodiacetic acid, 0.03 mol $Ba(OH)_2\cdot 8H_2O$ and 0.02 mol $CoSO_4\cdot 7H_2O$ in 50 ml of water, separating the $BaSO_4$ precipitate and following further the procedures for the isomeric potassium salts. The average yield was 65%

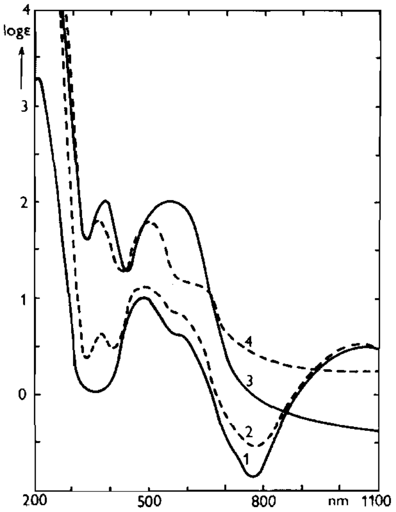

Fig. 1. Electronic absorption spectra of the bis-(iminodiacetato)cobalt(II) complexes (curve 1), sodium bis-(iminodiacetato)cobaltate(II) prepared according to Laitinen (curve 2) and of the *cis* (curve 3) and *trans* (curve 4) bis-(iminodiacetato)cobalt(III) complexes.

Trans-$Na[Co(ida)_2]\cdot 3H_2O$, *cis*-$Li[Co(ida)_2]\cdot 2.5H_2O$, *trans*-$Li[Co(ida)_2]\cdot H_2O$, *cis*-$H[Co(ida)_2]\cdot ½H_2O$ and *trans*-$H[Co(ida)_2]\cdot 4H_2O$ were prepared by conversion of a 0.05 *M* solution of the appropriate isomer of $Ba[Co(ida)_2]_2$ with a solution of the appropriate sulphate or of sulphuric acid. The complexes precipitated from the solution within several days at laboratory temperature. The average yields were 70%. The results of analyses of the compounds prepared are given in Table I.

Results and Discussion

For the preparation of the bis(iminodiacetato)-cobaltate(II) and (III) complexes, procedures obeying the equations,

$$Co^{2+} + 2(ida)^{2-} + 2M^+ \rightarrow M_2[Co(ida)_2]$$

$$Co^{2+} + 2(ida)^{2-} + M^+ \xrightarrow[0\,°C]{H_2O_2} cis\text{-}M[Co(ida)_2]$$

$$Co^{2+} + 2(ida)^{2-} + M^+ \xrightarrow[80\,°C]{H_2O_2} trans\text{-}M[Co(ida)_2]$$

were used. When basic cobaltous carbonate was used as the initial substance for the preparation of $Na_2[Co(ida)_2]$ according to Laitinen [6], the product obtained contained 2–5% Co^{3+} as can be seen from

TABLE I. Analytical and Physical Data.

Substance	Results of Analyses								Infrared spectra (cm^{-1})			Molar Susceptibility χ_M 10^{-3}
	%M		%Co		%N		$\%H_2O$		sym –COO–	antisym –COO–	N–H	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.				
cis-H[Co(ida)$_2$]·½H_2O			17.73	17.80	8.38	8.46	2.72	2.71	1375	1660	3200	–0.0538
trans-H[Co(ida)$_2$]·4H_2O			14.90	14.95	7.08	7.11	18.5	18.3	1375	1660	3200 3200	–0.225
cis-Li[Co(ida)$_2$]·2.5H_2O	1.86	1.86	15.77	15.79	7.52	7.51	12.6	12.1	1390	1650	3290	–0.042
trans-Li[Co(ida)$_2$]·H_2O	2.00	2.01	16.90	17.03	8.17	8.09	5.8	5.2	1390	1680	3220	–0.022
cis-NaCo[(ida)$_2$]·2H_2O	5.96	6.05	15.36	15.50	7.40	7.37	9.3	9.5	1385	1670 1650	3210	–0.025
trans-Na[Co(ida)$_2$]·3H_2O	5.62	5.77	14.68	14.80	7.15	7.03	13.4	13.6	1380	1670 1640	3210	–0.086
cis-K[Co(ida)$_2$]·2.5H_2O	9.51	9.66	14.49	14.54	7.06	6.91	10.7	11.1	1370	1660 1655	3185 3140	–0.056
trans-K[Co(ida)$_2$]·2H_2O	9.76	9.86	14.81	14.87	7.13	7.07	9.2	9.1	1375	1675	3185 3200	–0.050
cis-Ba[Co(ida)$_2$]$_2$·4.5H_2O	16.03	15.96	13.66	13.69	6.45	6.51	9.6	9.4	1390	1650	3260	–0.062
trans-Ba[Co(ida)$_2$]$_2$·5.5H_2O	15.69	15.63	13.37	13.41	6.47	6.38	11.3	11.3	1380	1650 1590	3220	–0.281
H_2[Co(ida)$_2$]·6H_2O			13.75	13.67	6.52	6.49	25.4	25.0	1405	1625	3270	7.79
Li_2[Co(ida)$_2$]·4H_2O	3.45	3.41	14.39	14.47	6.92	6.87	17.8	17.7	1410	1630	3305 3230	8.33
Na_2[Co(ida)$_2$]·7H_2O	9.41	9.32	12.11	11.95	5.80	5.68	26.0	25.6	1400	1620	3295	8.44
K_2[Co(ida)$_2$]·4H_2O	16.62	16.59	12.66	12.50	6.01	5.94	15.6	15.3	1410	1640	3310 3230	9.95
Ba[Co(ida)$_2$]·8H_2O	22.49	22.80	9.82	9.78	4.79	4.65	24.1	23.9	1405	1615	3300	8.82

TABLE II. Electronic Spectra.

Substance		Assignment		
		$^1A_{1g} \rightarrow {}^1T_{2g}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	
cis $H[Co(ida)_2] \cdot 0.5H_2O$		370	565	
$Li[Co(ida)_2] \cdot 2.5H_2O$		370	560	
$Na[Co(ida)_2] \cdot 2H_2O$		370	550	
$K[Co(ida)_2] \cdot 2.5H_2O$		370	560	
$Ba[Co(ida)_2]_2 \cdot 4.5H_2O$		370	560	
	CT	$^1A_{1g} \rightarrow {}^1B_{2g} + {}^1E_g$	$^1A_{1g} \rightarrow {}^1E_g$	$^1A_{1g} \rightarrow {}^1A_{2g}$
trans $H[Co(ida)_2] \cdot 4H_2O$	280 sh	365	495	605
$Li[Co(ida)_2] \cdot H_2O$	280 sh	365	495	620
$Na[Co(ida)_2] \cdot 3H_2O$	300 sh	360	500	620
$K[Co(ida)_2] \cdot 2H_2O$	285 sh	365	490	615
$Ba[Co(ida)_2]_2 \cdot 5.5H_2O$	270 sh	365	500	615
	$^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$H_2[Co(ida)_2] \cdot 6H_2O$	–	480 sh, 510	650 sh	
$Li_2[Co(ida)_2] \cdot 4H_2O$	440	470; 490 sh	590 sh	1050
$Na_2[Co(ida)_2] \cdot 7H_2O$	440 sh	470; 490 sh	560 sh	1050
$K_2[Co(ida)_2] \cdot 4H_2O$	430 sh	470 sh, 490	560	1050
$Ba[Co(ida)_2] \cdot 8H_2O$		480	560	1025

the reflectance spectrum (Fig. 1) and also found by the potentiometric titration. The procedure based on the above equations was unsuccessful for the preparation of the free acids and of *trans*-Na[Co(ida)$_2$] and $K_2[Co(ida)_2]$. With the sodium salt the Co(II) was not oxidized, yielding the product $Na_2[Co(ida)_2] \cdot 7H_2O$; with the potassium salt oxidation with atmospheric oxygen occured leading to a mixture of *cis* and *trans* isomers of $K[Co(ida)_2]$. Therefore, these substances were prepared by conversion of the barium salts with sulphuric acid or the appropriate sulphate.

Infrared Spectra

In the study of infrared spectra, our attention was directed toward valence vibrations of the carboxylic group and of the N–H group, from the point of view of the coordination of these groups to the central atom (Table I). The absorption band of the antisymmetric vibration of carboxylic group in the Co(III) complexes is shifted on average to a value of 1660 cm^{-1} and in the Co(II) complexes to a value of 1620 cm^{-1}. These shifts, together with the value of the difference in the wavenumbers of the symmetric and antisymmetric vibrational bands, indicate monodentate coordination of the carboxylic groups. Only with $H_2[Co(ida)_2]$ do the experimental absorption bands at 1590 and 1625 cm^{-1} also suggest the possibility of bidentate coordination of a carboxylic group, similar to $Cuida \cdot 2H_2O$ [8]. No band of the –COOH group was found in the region from 1700 to 1800 cm^{-1}.

The absorption bands of the N–H group valence vibration were shifted to lower values, on average by 130 cm^{-1} with the $M[Co(ida)_2]$ complexes and by 30 cm^{-1} with the $M_2[Co(ida)_2]$ complexes, compared with the K_2ida band wavelengths.

The shifts of the absorption bands of the antisymmetric valence vibration of carboxylic group an of the valence vibration of the N–H group correspond to coordination of both groups in both types of complexes, and are in agreement with the values obtained for analogous cobalt compounds [9, 10] and with the stability of the complexes in solution [5].

Magnetic Properties

The experimental molar susceptibilities for complexes of type $M[Co(ida)_2]$ (Table I) correspond to the assumption that all electrons in the complex ion are paired. The molar susceptibilities and the calculated values of the effective magnetic moment

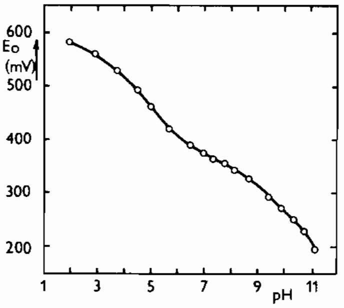

Fig. 2. Dependence of the redox potential, E, of the $[Co(ida)_2]^{2-}/[Co(ida)_2]^-$ system on the pH. The E_0 values are related to the hydrogen electrode.

for the $M_2[Co(ida)_2]$ (Table I) lie within the range observed for this type of substance [11].

Electronic Spectra

The diffusion reflectance spectra of the solid substances and the absorption electronic spectra of the aqueous solutions of the *cis* and *trans* isomers of the $M[Co(ida)_2]$ complexes are virtually identical. The bands in the reflectance spectra are shown in Table II. The absorption spectra are given in Fig. 1. The absorption spectrum of the *cis* isomer is in good agreement with that obtained by Jϕrgensen [12] for complex anion $Co(edta)^-$. From the value of 10 Dq calculated according to Lever [13] for both isomers it follows that 2 anions of iminodiacetic acid in *cis* configuration form a stronger field (*cis*-$[Co(ida)_2]^-$ 19660 cm^{-1}) than do 2 iminodiacetic acid anions in *trans* configuration (*trans*-$[Co(ida)_2]^-$ 18930 cm^{-1}). The electronic absorption spectra of aqueous solutions of the $M_2[Co(ida)_2]$ complexes are virtually independent of M. The diffusion reflectance spectra are identical, except for the absorption band of the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. Splitting of this band can be observed due to the crystal field. The assignment of the reflectance spectra bands is given in Table II. The absorption spectra are depicted in Fig. 1. In the spectra of the cobalt(II) complexes, the absorption spectra are depicted in Fig. 1. In the spectra of the cobalt(II) complexes, the absorption band of the $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition was not found. Therefore, the relationship [6, 13], 10 Dq = 5/4 ν_1, corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition (10 Dq = 13120 cm^{-1}), was used for the ligand field strength. In view of the intensity of the ν_1 band, the nitrogen atoms in the complex molecule are probably in the *trans* position, as in *cis* complexes the intensity of the ν_1 band is usually higher and the band is often split [13].

Redox Potential of the $Co(ida)_2^-/Co(ida)_2^{2-}$ Couple

The effect of the kind of cation on the oxidizability of $[Co(ida)_2]^{2-}$ with oxygen observed during preparations led us to the study of the $[Co(ida)_2]^-/[Co(ida)_2]^{2-}$ redox systems and of the stability of aqueous solutions of $M_2[Co(ida)_2]$. The dependence of the redox potential on the pH is shown in Fig. 2. The values obtained indicate that atmospheric oxygen cannot oxidize the complexes that have already been formed. The results of the polarographic study show that the $[Co(ida)_2]^-$ complexes are polarographically reduced in aqueous solutions in a single one-electron wave to $[Co(ida)_2]^{2-}$. The half-wave potentials are almost independent of the nature of the alkali metal cation and their values are between −0.01 and +0.01 V.

The study of the absorption spectra has shown that aqueous solutions of all the studied $M_2[Co(ida)_2]$ complexes, obtained by dissolving the complexes in water, are stable in the air at concentrations of 0.5 – 0.1 *M*. However, the absorption spectra of aqueous solutions prepared from the initial substances, *i.e.* iminodiacetic acid, alkali carbonate and cobalt(II) chloride, exhibit increasing intensity of the absorption band at 370 nm corresponding to Co(III) from Li^+ to Cs^+. The Co(III) fraction of the total cobalt content is 20, 35, 45, 50 and 75% for the salts of Li^+, Na^+, K^+, Rb^+ and Cs^+, respectively. Thus it follows from the absorption spectra that oxidation with atmospheric oxygen plays a role only during the formation of the complexes in aqueous solutions when water molecules in the coordination sphere are gradually substituted by carboxylic groups. In this process an effect of the alkali metal can be encountered, although the stability constants for complexes of iminodiacetic acid with alkali metals suggest the opposite effect [14]. Another explanation is the assumption of bridge formation between the complex anions through the alkali metal; this effect was observed in the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system [15].

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