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Synthesis and Characterization of *Trans*-bis(N-alkyliminodiacetato)chromium(III) Complexes

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Chromium complexes of the type K[Cr(RIDA)$_2$]·nH$_2$O, R = ethyl (E), n-propyl (n-P), isopropyl (i-P), n-butyl (n-B), and t-butyl (t-B), have been prepared in a one pot synthesis, omitting isolation of the ligands. The complexes have been characterized using infrared, visible–UV, and luminescence spectroscopy, and are all found to possess the trans *configuration. Band assignments have been made to electronic energy level schemes.*

Introduction

Iminodiacetate, $HN(CH_2COO^-)_2$, or IDA, forms very stable hexacoordinated complexes with a large number of transition metal ions [1–6]. It behaves as a tridentate ligand, adopting a facial configuration in *cis* or *trans* geometry with respect to the nitrogen atoms. A meridional isomer has not yet been identified. The N-alkyl derivatives, methyliminodiacetic acid (H_2MIDA) and ethyliminodiacetic acid (H_2EIDA), coordinate in a similar fashion, yielding with Co(III) and Cr(III) only complexes in the *trans* configuration [1, 2, 7, 8].

Molecular models do not reveal any obvious steric reasons that a *trans* arrangement should be preferred to a *cis*, although stereospecific coordination is not uncommon for Cr(III) complexes. We felt it would be of interest to examine Cr(III) complexes of higher homologs in this series, where steric effects will be more pronounced, both from the point of view of geometrical isomers formed, and with regard to variations in spectroscopic properties.

The traditional route to the alkyliminodiacetic acids, H_2RIDA, is the substitution reaction of α-chloroacetic acid with the corresponding primary amine, RNH_2, in alkaline solution to prevent quaternization of the amine. Increasing the length of the alkyl chain R tends to shift electron density towards the nitrogen, enhancing the nucleophilic character of the amine, and promoting the substitution reaction. The presence of the bulky alkyl groups, however, should hinder the approach of chloroacetic acid and affect the yield adversely.

Experimental

Syntheses

Uehara *et al.* [8], propose syntheses of alkyliminodiacetic acids which we find difficult to reproduce for some of the higher homologs. A simple isolation of the ligands from the side products and the bulk of KCl formed during the reaction, although easily obtained for MIDA, was not possible for the propyl and butyl homologs. Since we are primarily interested in the metal complexes, however, we did not pursue lengthy attempts at isolation, but rather continued with coordination to Cr(III) in the same solution.

The general synthesis was as follows: Chloroacetic acid (19 g, 0.2 mol) was dissolved in water (30 ml) and $KHCO_3$ (20 g, 0.2 mol) added with care. On cooling, 0.1 mol of alkylamine (*e.g.*, 6.5 g of 70% $C_2H_5NH_2$) was added dropwise into the solution, taking care to reduce evaporation of amine to a minimum. The reaction mixture was kept overnight, and any KCl present filtered off. The solution was warmed to 50 °C, 10 ml of 50% KOH added, and the solution reacted with small portions of an almost equivalent amount of $CrCl_3 \cdot 6H_2O$ (13.3 g, 0.05 mol). After refluxing for three hours the suspension was filtered hot, avoiding precipitation of KCl. Although some of the product is lost in this process, this procedure was found to be most convenient. The yields obtained for this synthesis were 24% for K[Cr(EIDA)$_2$], 26% for K[Cr(n-PIDA)$_2$], 13% for K[Cr(i-PIDA)$_2$], 7.5% for K[Cr(n-BIDA)$_2$], and 4.0% for K[Cr(t-BIDA)$_2$]. The corresponding yield of the MIDA complex, obtained for a two step procedure where the ligand was separated before synthesizing the complex, is calculated to be 29.7% relative to the starting material [2, 8].

The elemental analyses for these compounds are given in Table I, and are all within usual limits.

TABLE I. Elementary Analyses Found and Calculated (in parentheses) for $K[Cr(RIDA)_2]$ in Weight % for Substances Dried at about 110 °C.

R	C	H	N	Cr	K
E	35.3(35.2)	4.6(4.4)	6.8(6.9)	13.0(12.7)	8.9(9.6)
n-P	38.3(38.4)	5.3(5.0)	6.3(6.4)	12.0(11.9)	8.6(8.9)
i-P[a]	35.4(34.9)	5.8(5.6)	5.7(5.8)	10.5(10.8)	8.1(8.1)
n-B	40.5(41.3)	5.8(5.6)	5.6(6.0)	10.8(11.2)	8.0(8.4)
t-B[a]	37.8(37.6)	6.1(6.1)	5.4(5.5)	10.3(10.2)	7.7(7.7)

[a] 2.5 H_2O is contained. For the i-P compound two or three molecules of H_2O may also be calculated from the analytical results.

Physical Measurements

Infrared spectra were recorded in KBr pellets (concentration ∼0.5%) on a Perkin Elmer Model 457 spectrometer. Visible and near-UV absorption and reflectance spectra were obtained on a Cary 14 spectrophotometer with a Model 1411 reflectance attachment. Luminescence spectra were obtained with previously described instrumentation [9].

Results and Discussion

Ligand and Complex Synthesis

The decline in yield of the Cr(III) complexes proceeding from methyl- to t-butyliminodiacetic acid would seem to indicate that the steric hindrance from the bulky alkyl groups exerts a greater influence than the inductive effects from the same alkyl groups. However, steric effects are presumably more important in the complex formation step than in the displacement at carbon.

In each case the $[Cr(RIDA)_2]^-$ complex obtained was chromatographically pure, in that no band separation was observed upon elution in a Dowex 1-X8 column. Thus only one isomer resulted for each alkyl R.

Infrared Spectra

Some infrared data for the Cr(III) alkyliminodiacetate complexes are compiled in Table II. The assymmetric carboxylate stretching frequency is found at 1630–1645 cm^{-1}, shifted 60–120 cm^{-1} to lower energy from the corresponding free ligands, as is typical of coordinated carboxylate groups [7, 10, 11]. X-ray analyses of the IDA, i-PIDA, and t-BIDA complexes [12] have confirmed that all four carboxylate groups are coordinated, and water is present only as water of crystallization. This point is an important one, since coordination isomers have been observed by Vieles and Israily for the compounds $H[Cr(MIDA)_2]$ and $H[Cr(EIDA)_2]$. In this case violet isomers obtained contained coordinated water in place of carboxylate [7].

Electronic Spectra

Although all the complexes investigated are chemically rather similar, a pronounced difference in color is apparent. The MIDA, EIDA, n-PIDA, and n-BIDA complexes vary from orange to pink, while the IDA, i-PIDA, and t-BIDA complexes are a more deeply colored purple or violet. This somewhat unexpected grouping of the compounds is upheld by the diffuse reflectance and absorption spectra (see Table III), where it should be noted that the first spin-allowed transition, $^4A_{2g} \rightarrow {}^4T_{2g}$ (in O_h notation), gives rise to the absorption of highest intensity in the visible region. From this transition a maximum absorption at 19.7–21.2 kK is found for the pink to orange group of compounds, and an absorption in the region of 18.3–19.4 kK is found for the purple to violet group.

$[Cr(IDA)_2]^-$ is known to have the *cis* configuration, while the MIDA and EIDA complexes have been identified as *trans* [2, 7, 8]. A naive assignment of the RIDA complexes on the basis of first band maxima (which would indicate a *cis* structure for i-PIDA and t-BIDA complexes) is refuted by X-ray evidence that both the i-PIDA and t-BIDA complexes are *trans* with respect to the amines, while $[Cr(IDA)_2]^-$ is indeed *cis* [12].

Absorption spectra are more often used as a configurational probe through consideration of band splittings and intensities. A comparison with the energy level scheme obtained from ligand field theory or from the angular overlap model [14] (see Figure 1) shows that the splitting of the first spin-allowed octahedral level is larger for the *trans* than for the *cis* configuration, the more intense component of the band being located on the short wave length side because of its higher degeneracy. The low intensity component should remain at the position of the octahedral chromophore CrO_6, which compares well with the corresponding transition at 17.5 kK for the tris(oxalato) compound $[Cr(ox)_3]^-$ [15]. The splitting for the *cis* compound is smaller by a factor of two and is generally not observed under normal experimental conditions.

Although no splitting of the first band was observed for some of the higher homologs, no firm conclusions can be drawn from this, since the splittings observed for MIDA, EIDA, and n-PIDA complexes were not at all marked. The fact that splitting was observed for the latter three complexes does, however, point to a *trans* geometry for them.

All three purple compounds have a first band maximum near 19 kK, as does $[Cr(en)(ox)_2]^-$ (en = ethylenediamine), with a similar *cis*-CrN_2O_4 chromophore [16]. The extinction coefficients of the *cis* complexes, 75 M^{-1} cm^{-1} for $[Cr(IDA)_2]^-$ and 91

TABLE II. Antisymmetric Stretching mode $\bar{\nu}_{as}$ of Carboxylate Group for Free Ligands and for Complexes $Cr(RIDA)_2^-$ and Some Intense Characteristic Band Peaks in the Fingerprint Region, in cm^{-1}.

R	$\bar{\nu}_{as}$ (–COO⁻) Free Ligand	$\bar{\nu}_{as}$ (–COO⁻) Complex	Complexes, Fingerprint Region 600–1200 cm^{-1}
H	1715	1640	1080, 1013, 950, 908, 886, 737
M	1695	1640	1147, 1091, 1008, 978, 960, 931, 916, 894, 740
E	1705[a]	1640	1172, 1125, 1088, 1025, 954, 930, 913, 883, 824, 748, 735
n-P	1725	1640	1090, 1037, 977, 948, 930, 920, 898, 880, 768, 742, 622
i-P	1750	1630	1183, 1139, 1037, 987, 939, 914, 834, 753, 731
n-B	–	1645	1122, 1093, 1046, 1020, 963, 940, 926, 896, 763, 746
t-B	1730	1645	1185, 1086, 1058, 1039, 982, 945, 911, 860, 782, 760, 710, 632

[a] Ref. 7.

TABLE III. Ligand Field Energy Levels of $K[Cr(RIDA)_2]$ Complexes Obtained from Band Maxima in kK of Diffuse Reflectance and (in brackets) of Absorption Spectra in Aqueous Solution, Both at Normal Temperatures. sh indicates a band shoulder.

LF Levels in O_h Notation	R = H[a]	M[a]	E	n-P	i-P	n-B	t-B
^2E_g	14.3 (14.3)	14.7 (14.6)	14.7 (14.6)	14.7 (14.6)	14.7 (14.6)	14.7 (14.6)	14.6 (14.7)
$^2T_{1g}$	15.2	(15.4)	(15.4)	(15.4)	(15.4)	(15.4)	(15.4)
$^4T_{2g}$	18.9[b] (19.3)[c]	17.4sh[b] 21.2[b] (20.0)[c]	17.4sh 20.1 (20.0)	17.4sh 20.5 (20.0)	19.4 (18.9)	20.2 (19.7)	18.9 (18.3)
$^2T_{2g}$	22.5[b]	(23.8)[b]	23.1		22.5		22.2 (21.7)
$^4T_{1g}$	25.5[b] (25.6)[c]	28.3[b] (27.6)[c]	27.9 (27.8)	28.3 (27.8)	27.9 (27.3)	28.1 (27.7)	27.7 (27.2)

[a] Refer to sodium salts. [b] Ref. 11. [c] Ref. 2.

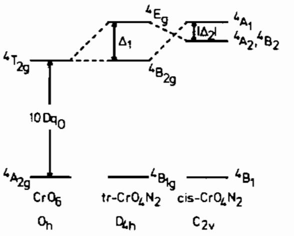

Figure 1. Term splitting scheme of the lowest spin allowed transitions for different symmetries ($\Delta_1 = 5\ (Dq_N - Dq_O)$, $\Delta_2 = -\Delta_1/2$).

M^{-1} cm^{-1} for $[Cr(en)(ox)_2]^-$, are appreciably larger than those for the *trans* complexes, with extinction coefficients around 45 M^{-1} cm^{-1}. This lower intensity is expected for the *trans* isomers, because of the presence of an inversion center, causing electric dipole transitions to be more strongly Laporte-forbidden. Since the first band extinction coefficients for all complexes investigated except the IDA lie near 45 M^{-1} cm^{-1}, the assumption of *trans* geometry for all would seem justified.

Luminescence Spectra

The *cis*-$[Cr(IDA)_2]^-$ and *trans*-$[Cr(MIDA)_2]^-$ complexes possess vastly different luminescent properties, apparently emitting from different electronic states [9, 17]. The spectrum of the *cis* complex at 85 °K consists of a broad fluorescence spectrum with, depending on conditions, a normal sharp line phosphorescence superimposed. The spectrum of the *trans* complex consists of an anomalous phosphorescence, with the region of maximum intensity displaced from the 0–0 line [18].

Luminescence spectra of all of the homologous compounds investigated here also evinced the pattern of anomalous phosphorescence exhibited by *trans*-$[Cr(MIDA)_2]^-$, the spectra being quite similar. Since the geometric requirements for observation of such anomalous phosphorescence behavior appear to be quite stringent, the conclusion that all these complexes are *trans* appears to be strongly supported. An analysis of the luminescence spectra will appear elsewhere.

Bond Lengths and Ligand Field Parameters

The somewhat unusual ligand field spectroscopical behavior of the higher homolog complexes can be explained from increasing Cr–N distances (IDA 2.05–2.10Å, i-MIDA 2.12Å, t-BIDA 2.15Å) due to larger steric effects [12]. Larger internuclear distances simulate smaller ligand fields (a point charge model in first approximation yields an R^{-5} dependence on the Cr–N distance) and therefore the ligand field strengths may approach more closely those of oxygen donor ligands [19]. The splitting of the octahedral $^4T_{2g}$ level by a ligand field of symmetry D_{4h} is, in terms of the parameter Dt,

$$E(E_g) - E(B_{2g}) = \frac{35}{4}Dt \qquad (1)$$

(if only diagonal elements of the perturbation matrix are considered [20, 21] and Dt can be expressed in terms of the octahedral ligand field parameter Dq as

$$Dt = -\frac{4}{7}(Dq_O - Dq_N) \qquad (2)$$

This splitting must decrease as the two parameters, the carboxylate Dq_O and the amine group Dq_N, tend toward each other. From these equations the Dq_N parameter is calculated to be 2.28–2.50 kK in alkyliminodiacetates, using the observed $^4T_{2g}$ components given in Table III. This compares with the corresponding octahedral ligand field parameter of the $[Cr(en)_3]^{3+}$ complex, which is Dq_N = 2.19 kK [15]. For *cis* complexes the factor in Eq. (2) for Dt is +2/7, yielding a splitting of the $^4T_{2g}$ level which is smaller by a factor of two compared to *trans* isomers, if equal metal–ligand distances are assumed. A band splitting for *cis*-IDA which is half as large as for the *trans*-MIDA complex, *i.e.*, smaller than 2 kK, may not be resolvable under normal conditions.

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