complexes. pk_a is calculated to be 9.11 and 8.71 for the TML–cysteine and TML–penicillamine complexes, respectively. These constants are both similar in magnitude to the microconstant pk_{13} for cysteine and penicillamine, suggesting that the TML cation complexed to the sulfhydryl group closely mimics a similarly bonded hydrogen ion, in terms of its effect on the acid strength of the neighboring ammonium groups.

Because of the one-coordinate nature of TML, chemotherapeutic ligands which are successful for the treatment of inorganic lead poisoning are not necessarily going to be effective for treating trialkyllead poisoning. For example, penicillamine is an effective treatment in inorganic lead poisoning; however, it was found to have little effect on intoxication due to trialkyllead compounds.[3] On the assumption that the ligand must form a complex with the trialkyllead species

to be an effective treatment, this is as would be predicted from the results of this study; the conditional formation constants for the TML–cysteine and TML–glutathione[24] complexes at pH 7 are 3.8×10^3 and 3.6×10^3 as compared to 1.2×10^3 for the TML–penicillamine complex.

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# L-Histidine Complexes of Chromium(III)

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Two isomers of bis(L-histidinato)chromium(III), in which histidine functions as a tridentate ligand, have been prepared and characterized. In addition, a partially characterized di-μ-hydroxy-bis(L-histidinato)dichromium(III) complex is described. A simple angular overlap model calculation on the electronic spectra of the two $[\text{Cr}(\text{L-his})_2]^+$ isomers, together with data from another amino acid complex, yields values for the ligand field splitting parameter Δ (or $10Dq$) of 22.7×10^3, 21.1×10^3, and 17.1×10^3 cm^{-1} for the amine, imidazole (N^3), and carboxylate ligands, respectively. The sharp-line luminescence of the trans(imidazole) isomer of $[\text{Cr}(\text{L-his})_2]^+$ is also reported.

Introduction

Complexes of L-histidine with a wide variety of metal ions have been characterized. In bis complexes, histidinate often functions as a tridentate ligand[1-7] but, as with certain Cu(II) and Pt(II) complexes, may be bidentate, with the imidazole or carboxylate group uncoordinated.[8,9] A review article on transition-metal complexes with tridentate amino acids appeared in 1975.[10]

There have been no reports of tris complexes, in which histidine would presumably be bidentate, but bidentate coordination may be exhibited in binuclear complexes, some of which are of interest as oxygen carriers.[11]

An octahedral bis complex with tridentate L-histidine, in which each histidine coordinates facially, can assume three isomeric forms

trans(imidazole)   trans(carboxylate)   trans(amine)
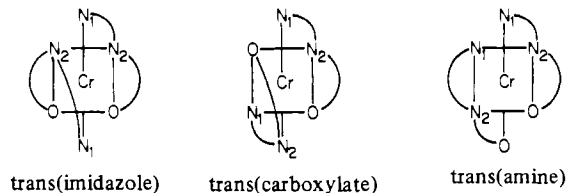
(here N$_1$ represents imidazole, N$_2$ amine, and O carboxylate). The trans(imidazole) isomer appears to be favored among the

first-row divalent cations whose crystal structures have been determined,[1-3,7] although both Zn(II) and Cd(II) form very distorted complexes, so that the orthoaxial representations above are inappropriate. All three isomers with Co(III) have been characterized,[12-14] the trans(imidazole) being predominant in the synthesis.

References to Cr(III) complexes with histidine are scant, consisting of our own preliminary report[15] and a doctoral dissertation by Grouhi-Witte,[16] in which bis complexes were prepared in solution only. We report here the characterization of the trans(imidazole) and trans(carboxylate) isomers of $[\text{Cr}(\text{L-his})_2]^+$ and the partial characterization of a binuclear complex, $[\text{Cr}_2(\text{L-his})_4(\text{OH})_2]$.

Experimental Section

trans(Imidazole)-[Cr(L-his)$_2$](NO$_3$). To a solution of NaOH (8.0 g, 0.2 mol) in water (125 mL) was added L-histidine (31 g, 0.2 mol) and Cr(NO$_3$)$_3$·9H$_2$O (40 g, 0.1 mol). The solution was heated on a steam bath for 8 h, during which time a fine reddish violet precipitate formed and then disappeared. The volume was allowed to sink to 50 mL, and orange-red crystals began to deposit. After cooling and filtration, 7 g of product was obtained. This was recrystallized by dissolving in water (60 mL), evaporating to 25 mL, and refrigerating overnight. The crystals obtained (4 g) were washed with water and ethanol and air-dried. Anal. Calcd for [Cr(C$_6$H$_8$N$_3$O$_2$)$_2$](NO$_3$): C, 34.1; H, 3.8; N, 23.2; Cr, 12.3. Found: C, 33.8; H, 4.1; N, 23.1; Cr, 12.3. The crystals were almost insoluble in ethanol, only slightly soluble in cold water, but quite soluble in warm water. Dissolved in water, it eluted as one band on a cation-exchange column (Dowex 50W-X8).

trans(Carboxylate)-[Cr(L-his)$_2$](ClO$_4$). The mother liquor from the above synthesis could be separated into two isomers (plus one or

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more neutral complexes eluting with the solvent front) on a cation-exchange column, a red band preceding the larger orange band representing the trans(imidazole) isomer. But separation characteristics were better when isomer mixtures were produced by boiling a solution of the trans(imidazole) isomer in water with activated charcoal (15 min), cooling quickly in ice, and filtering off the charcoal.

A 40 mm diameter jacketed column was filled with CM-Sephadex C-25 cation-exchanger to a depth of 30 cm. Ice water was circulated to retard isomerization of the red isomer, which makes itself visible as an orange trail from the red band at room temperature. The isomer mixture was loaded to a depth of 4 cm, and water was passed through the column, eluting a pale pink material. The main elution was carried out with 0.02 M NaClO₄. The red band separated cleanly ahead of the orange, whose R_f was 0.7 referred to the red band. A small purple band remained in some cases and was not eluted. The total elution time was 6–8 h.

The red band was concentrated from 1100 to 5 mL on a rotary evaporator at 15 °C, loaded onto a Sephadex G-10 column (20 mm × 20 cm), and eluted with water to effect a partial desalting. A pale pink band again separated ahead of the main body of material. The eluant containing the red complex was evaporated from 10 to 4 mL. Ethanol was added dropwise until the solution turned cloudy. It was then heated slightly until clear. This process was repeated twice, and the solution was cooled in ice. Long, red snakelike crystals began to form almost immediately. The crystals were collected, washed with ethanol, and dried in vacuo. Anal. Calcd for [Cr(C₆H₈N₃O₂)₂]-(ClO₄)·0.5H₂O·0.5C₂H₅OH·0.5NaClO₄: C, 28.2; H, 3.65; N, 15.2; Cl, 9.6. Found: C, 28.1; H, 3.7; N, 15.0; Cl, 9.8. We were not successful at eliminating NaClO₄·H₂O, and it is possible that it cocrystallized stoichiometrically. The visible absorption spectrum of the solid product in water matched that of the solution fresh from the ion-exchange column. It was very soluble in cold water but insoluble in ethanol.

[(L-his)₂Cr(OH)₂Cr(L-his)₂]. The hydroxy-bridged binuclear complex can exist in a very large number of isomeric forms. When a stoichiometric mixture of Cr(III) salt, L-histidine, and NaOH in water was heated for 3 h, a solution was obtained, the bulk of which passed through both anion- and cation-exchange columns. The absorption spectra of such solutions were not reproducible (λ^1_{max} = 510–525 nm), probably because several isomers were present. Upon standing, precipitates formed, the spectra of which were also not reproducible, although the empirical formulas worked out to [Cr(L-his)₂(OH)].

A complex of this formula with reproducible visible, IR, and luminescence spectral characteristics could be made by dissolving 10 g of *trans*(imidazole)-[Cr(L-his)₂](NO₃) in water (50 mL), which required heating to 60 °C. This solution was passed through an anion-exchange column (Dowex 1-X8, 30 mm × 25 cm) in OH⁻ form while still warm. Elution was with warm (35 °C) water over a period of 20 min. A precipitate began to form during collection. The eluant was refrigerated for 30 min and then filtered. The pink precipitate was dried in vacuo; yield 5 g. Anal. Calcd for [Cr₂(C₆H₈N₃O₂)₄-(OH)₂]·6H₂O: C, 33.4; N, 19.5; H, 5.4. Found: C, 33.1; N, 19.3; H, 5.4.

The above reaction was found to be reversible. Acidifying with 1 equiv of HCl yielded *trans*(imidazole)-[Cr(L-his)₂]⁺. The solid [Cr₂(L-his)₄(OH)₂] was almost insoluble in cold water, but was slightly soluble in warm (60 °C) water. The complex was neutral: it could be eluted with water from cation- and anion-exchange resins. Evidence that the complex was binuclear came from gel chromatography on Sephadex G-10. [Cr₂(L-his)₄(OH)₂] was eluted ahead of the trans(imidazole) isomer of [Cr(L-his)₂](NO₃) when the two were mixed. The R_f values with respect to the solvent front were approximately 0.7 and 0.4, respectively.

The ion-exchange procedure used to prepare [Cr₂(L-his)₄(OH)₂] from the trans(imidazole) isomer of [Cr(L-his)₂]⁺ did not work with the trans(carboxylate) isomer. Instead, the complex acquired a negative charge and adhered to the resin. However, simple addition of 1 equiv of base to the trans(carboxylate) isomer did yield a pink precipitate, whose properties were different from those of the binuclear complex already described. This complex was virtually insoluble in warm water. This material was not felt to be uniform and was not further characterized.

The bis(histidinato) complexes exhibited uncharacteristically rapid reactions to both bases (as described above) and acids, exhibiting immediate, substantial (up to 40 nm) shifts in absorption spectra peak

Table I. Vibrational Data (cm⁻¹) for Chromium(III)–Histidine Complexes

Carboxylate Frequencies		
	ν_{as}(COO)	ν_s(COO)
orange[a]	1614 vs, 1640 sh	1359 s[c]
red[b]	1640 vs	1368 s
dimer	1595 w, 1628 vs	1358 s, 1390 w

Amine Frequencies		
	δ(NH₂)	ρ_t(NH₂)
orange[a]	1562 m, 1590 vw	1187 m
red[b]	1568 m	d
dimer	1572 m	1176 s

Imidazole Frequencies			
	in-plane ring	ring breathe	in-plane C–H bend
orange[a]	982 m	1021 m, 1040 m	1082 s
red[b]	982 w	1025 w	d
dimer	990 w	1031 m	1070 s
histidinate (soln)[e]		1012 m	1097 sh

[a] [Cr(L-his)₂](NO₃). [b] [Cr(L-his)₂](ClO₄). [c] Possibly other bands obscured by NO₃⁻. [d] Obscured by ethanol. [e] Reference 18.

positions. This behavior was not explored in detail.

Instrumentation. Visible and UV absorption spectra were measured on a Cary 14 spectrophotometer, which, with a Model 1411 attachment, was also used to obtain reflectance spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer, using KBr disks, and on a Beckman FIR-720 interferometer (50–450 cm⁻¹), using pressed polyethylene disks. Circular dichroism spectra were obtained on a Cary 60 spectrometer.

Luminescence spectra on powdered samples at 85 K were obtained with a previously described apparatus,[17] which included a Spex 1700-II monochromator and a liquid-nitrogen-cooled photomultiplier tube with S-1 characteristics. Excitation was provided by the 366- or 436-nm line from a 100-W mercury lamp.

Elemental analyses were performed by Galbraith Analytical Laboratories.

Results and Discussion

A. Assignment of [Cr(L-his)₂]⁺ Isomers. During separation by cation-exchange chromatography, the red isomer was eluted first. This behavior is consistent with a trans(carboxylate) configuration which would result in a substantially lower dipole moment than would either of the isomers in which the carboxylates are cis. All three [Co(L-his)₂]⁺ isomers have been prepared,[14] with the elution order trans(carboxylate), trans(imidazole), trans(amine). Typical yields of the trans(amine) isomer were around 5% of the total [Co(L-his)₂]⁺, while 75% was trans(imidazole). This also points to the conclusion that the orange [Cr(L-his)₂]⁺ isomer is trans(imidazole) as well.

Coordination. In both [Cr(L-his)₂]⁺ isomers in the solid state, tridentate coordination through amine, imidazole (N³), and carboxylate groups is indicated by the small number (or lack) of solvents of crystallization. Infrared spectra (Table I) can also be used to demonstrate coordination by the groups in question. The antisymmetric and symmetric carboxylate stretching frequencies are shifted upward and downward, respectively, from 1579 and 1413 cm⁻¹, the value for the histidinate ion in solution.[18] These shifts are characteristic of carboxylate coordination.[19]

Smaller shifts in several ring deformation modes have been taken to indicate coordination of the imidazole group. In particular, the appearance of a moderately intense component

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Table II. Absorption and Circular Dichroism Spectra of Chromium(III)–Histidine Complexes

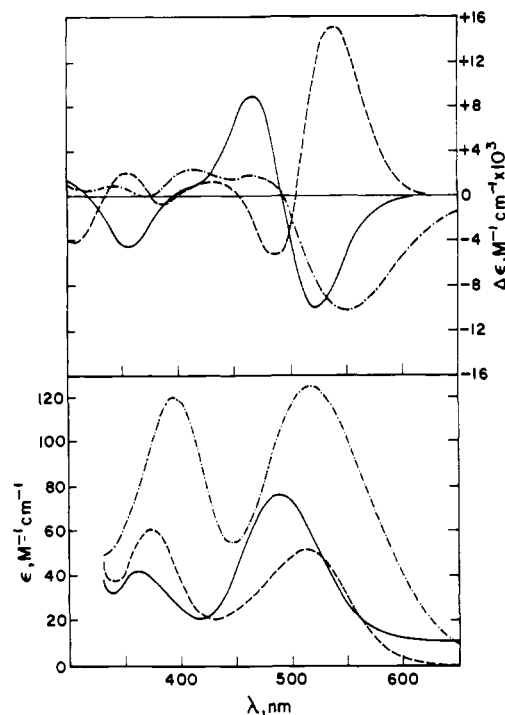| complex	band I		band II	
	abs λ_{max}, nm (ϵ)	CD λ_{max}, nm ($\Delta\epsilon$)	abs λ_{max}, nm (ϵ)	CD λ_{max}, nm ($\Delta\epsilon$)
trans(imidazole)-[Cr(L-his)$_2$](NO$_3$) (orange isomer)	488 (67)	514 (−0.010) 468 (+0.009)	363 (27)	355 (−0.005)
trans(carboxylate)-[Cr(L-his)$_2$](ClO$_4$) (red isomer)	513 (44)	537 (+0.015) 487 (−0.005)	373 (48)	438 (+0.0012) 384 (−0.0006) 355 (+0.002)
[Cr(L-his)$_2$(OH)]$_2$	517 (128)	550 (−0.010) 466 (+0.009)	394 (121)	411 (+0.002) 345 (+0.001)

Figure 1. Absorption (bottom) and circular dichroism spectra for chromium(III) complexes with L-histidine: *trans*(imidazole)-[Cr(L-his)$_2$(NO$_3$), —; *trans*(carboxylate)-[Cr(L-his)$_2$](ClO$_4$), - - -; [Cr$_2$(L-his)$_2$(OH)$_2$, -··-.

of an in-plane ring deformation in the region 965–980 cm^{-1} has been noted in a series of histidine complexes with divalent metal ions.[18] From the data in Table I, we conclude that imidazole is coordinated in both isomers.

Amine coordination is somewhat more difficult to determine with certainty. Oki[20] has demonstrated with chromium–amino acid complexes that the δ(NH$_2$) mode is shifted from 1505 to about 1600 cm^{-1} upon coordination. Another mode, probably an NH$_2$ twisting vibration,[21] was shifted from ca. 1110 to ca. 1190 cm^{-1}.[20] There are bands in the appropriate locations in the IR spectrum, which we assign in Table I to the bending and twisting modes of coordinated amine.

Spectroscopic Evidence. Compared to the IR spectrum of the orange isomer, that of the red isomer exhibits only about half the number of bands. This may be taken as further indication that the red isomer has the trans(carboxylate) geometry, which is, at least near the chromium atom, more symmetrical.

Electronic absorption spectra provide further confirmation of the isomer assignment. Spectral data are listed in Table II, and the spectra are shown in Figure 1. No splitting was evident in either spectrum; however, the first band in the

Table III. Absorption Spectra of Some CrN$_4$O$_2$ and CoN$_4$O$_2$ Chromophores[a]

compd	λ_{max}^1, nm	λ_{max}^2, nm	ref
trans(O)-[Cr(EDMA)$_2$]$^+$	505, (461)	380	b
trans(O)-[Co(EDMA)$_2$]$^+$	530, (454)	355	b
cis(O)-[Co(EDMA)$_2$]$^+$	500, (465)	346	b
trans-[Co(NH$_3$)$_2$(EDDA)]$^+$	536, (461)	364	c
cis-[Co(NH$_3$)$_2$(EDDA)]$^+$	500	358	c
trans(imidazole)-[Co(L-his)$_2$]$^+$	500	NR	d
trans(amine)-[Co(L-his)$_2$]$^+$	485	NR	d
trans(carboxylate)-[Co(L-his)$_2$]$^+$	535	350	d

[a] Key: EDMA = ethylenediaminemonoacetate; EDDA = ethylenediaminediacetate; L-his = L-histidine; NR = not reported. The wavelengths in parentheses represent shoulders. [b] Y. Fujii, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **43**, 786 (1970). [c] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965). [d] References 14 and 34.

spectrum of the red isomer is seen to be unsymmetrical, indicating the presence of a small peak under the envelope on the high-energy side. The apparently greater splitting in the red isomer may be taken as evidence of trans(carboxylate) geometry. The first band splitting in a *cis*-CrN$_4$O$_2$ or -CoN$_4$O$_2$ chromophore would be expected to be about half that in the trans isomer.[22] The ligand field strength of the histidine imidazole nitrogen has been found to be intermediate between amine nitrogen and carboxylate[23,24] which reduces the magnitude of the expected splittings, especially in the trans(imidazole) isomer.[13]

In accordance with theory, the smallest splitting exhibited among [Co(L-his)$_2$]$^+$ complexes was from the trans(imidazole) isomer,[12] a result consistent with the assignment of the trans(imidazole) geometry to the orange [Cr(L-his)$_2$]$^+$ isomer, because of its quite symmetrical band shapes.

An argument based on the actual positions of the band maxima is somewhat riskier, since the relative peak positions in cis and trans isomers depend on bandwidths (which affect the extent to which the splitting is observable), as well as on other factors. However, a simple angular overlap model analysis (vide infra) predicts higher wavelength absorption maxima for the trans(carboxylate) isomer, and an examination of the spectra of analogous Cr(III) and Co(III) complexes in Table III confirms that for trans(carboxylate) isomers both bands are in general found at higher wavelengths than in the cis complexes. This again is consistent with the assignment of the red isomer of [Cr(hist)$_2$]$^+$ as trans(carboxylate).

Circular dichroism spectra are displayed in Figure 1 and Table II. It is seen that two isomers have opposite Cotton effects in the first band, with a greater molar ellipticity evinced by the red isomer. Arguments have been advanced, using molecular models, that the magnitude of $\Delta\epsilon$ should correlate with the degree to which a given molecule departs from an arrangement which would produce something like a plane of

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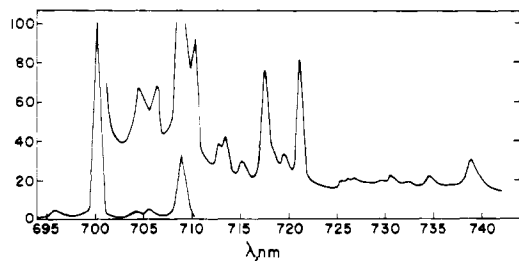
Figure 2. Luminescence spectrum of *trans*(imidazole)-[Cr(L-his)$_2$](NO$_3$) at 85 K. Excitation was at 436 nm on microcrystalline samples. Intensity is in arbitrary units.

symmetry.[25] Although appealing, such arguments have been shown to yield fallacious results with tridentate amino acid complexes.[26]

Similarly, arguments relating the sign of the dominant Cotton effects to the ordering of the nominal $^4B_2$ and ^4E excited states (from the octahedral $^4T_{2g}$) cannot be used reliably. This is well illustrated by the [Co(L-his)$_2$]$^+$ analogues. The trans(amine) and trans(imidazole) isomers, both of which should have a $^4A_2$ lowest excited state in the D_{4h} holohedrized symmetry,[13] exhibited opposite Cotton effects in the lowest energy visible bands.[14]

There remains the simple empirical analogy with the cobalt(III) analogues. The trans(imidazole) and trans(carboxylate) isomers of [Co(L-his)$_2$]$^+$ exhibit a mirror image type of relationship as in Figure 1, the trans(imidazole) isomer exhibiting a negative Cotton effect in the lowest energy band.[14] This again tends to confirm the [Cr(L-his)$_2$]$^+$ assignments above.

The orange isomer exhibits at 85 K a sharp line luminescence spectrum typical of $^2E_g \rightarrow {}^4A_{2g}$ (in O_h) phosphorescence in Cr(III) complexes.[27] This spectrum is illustrated in Figure 2. The red isomer exhibits a broad $^4T_{2g} \rightarrow {}^4A_{2g}$ fluorescence, with a maximum (uncorrected) at 756 nm and a half-width of 900 cm^{-1}. Such behavior is not uncommon among amine–carboxylate complexes of Cr(III). The iminodiacetato and (methylimino)diacetato complexes, [Cr(IDA)$_2$]$^-$ and [Cr(MIDA)$_2$]$^-$, which have cis and trans geometries, respectively, exhibit at 85 K fluorescence and phosphorescence spectra, respectively.[17] If a translation from CrN$_2$O$_4$ to CrN$_4$O$_2$ chromophores is possible, we would expect similar behavior for [Cr(IDA)$_2$]$^-$, where the nitrogens are cis, and *trans*(carboxylate)-[Cr(L-his)$_2$]$^+$. Schläfer's rules[28] lead one to expect fluorescence to dominate as the first absorption band tends to longer wavelengths, representing the competition between ^2E and $^4T_2$ states. Although application of these rules to lower symmetry complexes is somewhat less certain, it should be noted that both the [Cr(IDA)$_2$]$^-$ and *trans*(carboxylate)-[Cr(L-his)$_2$]$^+$ isomers show longer wavelength absorption than their isomeric counterparts.

B. The Binuclear Complex. There are, of course, numerous isomers of [(L-his)$_2$Cr(OH)$_2$Cr(L-his)$_2$] possible, even on the assumption that one knew which histidine moieties remained coordinated. A dominant consideration in this respect is the speed of the reaction. Quite in contrast to typical Cr(III) ligand displacement reactions, the addition of hydroxide ion to *trans*(imidazole)-[Cr(L-his)$_2$]$^+$ in solution at room temperature produced a virtually instantaneous reaction, the color changing from orange to red and a precipitate forming. A similarly rapid reaction occurred when the [C(L-his)$_2$]$^+$ so-

lution was acidified, yielding a red-violet solution with a probable charge of 2+ from its cation-exchange characteristics. This latter compound could not be isolated in solid form. The trans(carboxylate) isomer of [Cr(L-his)$_2$]$^+$ underwent similarly rapid reactions with base.

Such a rapid reaction, releasing two coordination positions to hydroxides, must at least leave the remaining four positions intact. In addition the carboxylates could not yield their coordination sites without placing a negative charge on the complex. In order to coordinate two bridging hydroxides, then, two of the nitrogens cis to each other would have to be displaced. If this line of reasoning is correct, it would mean that, since we started with the imidazoles in the trans position, both imidazoles could not be dissociated.

Spectroscopic Evidence. Infrared spectral data (Table I) support the coordination of all carboxylate groups. They also tend to support the continued coordination by both the amine and imidazole nitrogens. In particular, the coordinated imidazole in-plane ring deformation appears at 990 cm^{-1}, and the δ(NH$_2$) mode is at 1572 cm^{-1} (vide supra), much as in the [Cr(L-his)$_2$]$^+$ complexes.

Hydroxy-bridged compounds have been identified from IR spectra by a δ(M–O–H) band near 950 cm^{-1}.[29,30] For [Cr(L-his)$_2$(OH)]$_2$ the only band in that immediate area without a counterpart in the spectrum of [Cr(L-his)$_2$]$^+$ is at 920 cm^{-1}. The Cr–O stretching frequency is probably more useful in the characterization of hydoxy-bridged compounds. The ν(Cr–O) band has been found at 550 and 547 cm^{-1} with considerable intensity in compounds of the type [Cr(bpy)$_2$OH]$_2^{4+}$, where bpy = 2,2'-bipyridine.[31] This mode can be assigned to the strong band at 530 cm^{-1} in the [Cr(L-his)$_2$(OH)]$_2$ spectrum.

The shifts to longer wavelengths in the electronic absorption spectrum (Figure 1) on going from [Cr(L-his)$_2$]$^+$ to [Cr(L-his)$_2$(OH)]$_2$ are consonant with replacement of nitrogen ligands by hydroxide. The larger shift in the second band is especially characteristic of hydroxide, the large π-donating ability of which makes itself felt in the $^4A_2 \rightarrow {}^4T_1$ transition.[32] A reflectance spectrum of the binuclear complex exhibited peaks at 514 and 393 nm, indicating by its similarity to the aqueous absorption spectrum that the complex dissolves intact.

A similar shift to a longer wavelength fluorescence spectrum (Figure 2) also indicates replacement by ligands lower on the spectrochemical series. The CD spectrum (Figure 1) resembles that of *trans*(imidazole)-[Cr(L-his)$_2$]$^+$ in the first band, though not in the second.

We infer from the infrared spectrum that, since amine and imidazole both appear to be coordinated, one of each (per chromium) have been displaced by hydroxide. The three electronic spectral techniques discussed above cannot be used for confirmation, because the difference in ligand field strength of the two nitrogen ligands is not large enough (vide infra), so that this conclusion must remain a tentative one. The two noncoordinated groups could belong to different histidine molecules or to one, which would leave the other tridentate.

A stoichiometrically indistinguishable alternative to a hydroxy-bridged binuclear complex is a mononuclear bis(histidine) complex in which one histidine has been deprotonated at the imidazole (N^1) nitrogen. Deprotonation of some histidine complexes has been shown to occur in solution at high pH.[18] We reject this interpretation on the grounds that a change of imidazole to imidazolate would not be likely to cause a large shift to lower energy in the absorption spectrum. A

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further possibility which cannot be neglected is that the histidine molecule is involved in bridging. The large number of known dihydroxy-bridged binuclear complexes, however, make this a less attractive alternative.

C. Angular Overlap Model. A simple analysis of the electronic absorption spectra of the three complexes can be made by using the angular overlap model,[33] neglecting off-diagonal terms and neglecting the mixing of t_{2g} and e_g levels due to deviations from orthoaxiality. Lacking any splitting in the absorption spectra, we make the assumption that the lowest energy observed absorption maximum is that of the doubly degenerate (or nearly so) component of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. The energy of this transition can be expressed in terms of the ligand field splitting parameters Δ_O, $\Delta_{N(a)}$, $\Delta_{N(i)}$, which represent the splitting which would arise from hypothetical octahedral Cr(III) complexes with carboxylate, amine, and imidazole ligands, respectively. For the bis(histidinato) complexes we may calculate[13,34] for the trans(imidazole) isomer

$$\Delta E = \frac{1}{2}\Delta_{N(i)} + \frac{1}{4}\Delta_{N(a)} + \frac{1}{4}\Delta_O = 20.5 \times 10^3 \text{ cm}^{-1} \qquad (1)$$

and for the trans(carboxylate) isomer

$$\Delta E = \frac{1}{2}\Delta_O + \frac{1}{4}\Delta_{N(i)} + \frac{1}{4}\Delta_{N(a)} = 19.5 \times 10^3 \text{ cm}^{-1} \qquad (2)$$

(See Table II.)

In order to solve for all three unknown quantities we may add spectral data for the facial isomer of tris(glycinato)-chromium(III), which has an absorption maximum at 503 nm.[35] The appropriate equation for Cr(gly)₃ is[33]

$$\Delta E = \frac{1}{2}\Delta_O + \frac{1}{2}\Delta_{N(a)} = 19.9 \times 10^3 \text{ cm}^{-1} \qquad (3)$$

Solving these equations simultaneously leads to parameter values

$$\Delta_{N(a)} = 22.7 \times 10^3 \text{ cm}^{-1}$$

$$\Delta_{N(i)} = 21.7 \times 10^3 \text{ cm}^{-1}$$

$$\Delta_O = 17.1 \times 10^3 \text{ cm}^{-1}$$

These values are in quite good agreement with those calculated for cobalt(III)–histidine complexes.[34]

Looking at the binuclear complex, with the assumption, as stated above, that the coordination sphere consists of two carboxylate, one imidazole, one amine, and two hydroxide ligands, we conclude that all three components of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition would have different energies. Still, if the peak position is assumed to correspond to an average of the three components, a value for Δ_{OH} of $19.0 \times 10^3 \text{ cm}^{-1}$ is obtained. A considerable uncertainty must attach to this, but it may be compared to values of 14.2 and $18.0 \times 10^3 \text{ cm}^{-1}$ obtained for nonbridging hydroxide in two chromium–amine complexes.[32]

D. Vibronic Spectrum. The sharp-line luminescence spectrum (Figure 2) observed at 85 K for the trans(imidazole) isomer of $[Cr(L\text{-}his)_2]^+$ can also be used to characterize the coordination environment. The vibronic data are collected in Table IV along with far-infrared data. The complementarity of the two techniques is strikingly apparent in Table IV—bands which are most intense in the IR (generally metal–ligand stretching modes) are weak or even absent in the vibronic spectrum, whereas intense vibronic peaks (predominantly ring deformations) are usually weak in the infrared spectrum.[31,36]

The two intense vibronic bands at 182 and 211 cm⁻¹ appear characteristic of amine–carboxylate complexes of Cr(III), representing ring deformation with a considerable $\delta(N\text{-}Cr\text{-}O)$

Table IV. Vibrational Data to 600 cm⁻¹ for
trans(Imidazole)-[Cr(L-his)₂](NO₃)

luminescence[a]		infrared[b]
$\nu_0 - \nu$	I^c	
98	9	97 m
132	7	
		157 s
182	29	179 vw
211	10	209 vw
		219 w
261	2	266 s
276	5	
308	2	304 w
		339 s
356	10	353 s
		373 vs
391	0.8	389 vs
424	7	425 s
		458 s
		469 m
502	vw	504 vs
519	vw	519 vs
		578 vs
585	vw	586 vs

[a] 85 K; $\nu_0 = 14\,282 \text{ cm}^{-1}$, values are $\pm 2 \text{ cm}^{-1}$. [b] Room temperature. [c] Intensity relative to the 0–0 band = 100.

character. Similarly the 356-cm⁻¹ band (353 cm⁻¹ in the 298 K IR) corresponds to the carboxylate bending mode, $\delta(OCO)$, as observed in other Cr(III) complexes.[31] As a ring deformation, this too acquires considerable intensity in the vibronic spectrum. Metal–oxygen stretching modes have been noted to be more intense in luminescence than metal–nitrogen modes.[36] Thus the 424-cm⁻¹ band (425 cm⁻¹ in IR), although relatively intense, may be considered to have substantial ν-(Cr–O) character. The observed frequency agrees well with ν(Cr–O) frequencies in other chromium(III)–carboxylate complexes[31] and no doubt acquires much of its vibronic intensity through mixing with ring deformations.

The metal–amine and metal–imidazole stretching modes are less easily recognized but are probably found at respectively higher[13,37] and lower[38] frequencies than ν(Cr–O).

E. General Discussion. The trans(imidazole) and trans-(carboxylate) isomers of $[Cr(L\text{-}his)_2]^+$ appear to be quite well characterizable through the various spectroscopic techniques applied. No evidence was found for the trans(amine) isomer. We expected this isomer would have ion-exchange properties similar to those of the trans(imidazole) complex, but electronic spectra of the leading and trailing edges of the trans(imidazole) band on CM Sephadex or Dowex 50W-X8 showed the band to be homogeneous.

Grouhi-Witte,[16] on the other hand, has claimed separation of all three isomers on a Sephadex cation-exchange column, without, however, being able to crystallize any of the fractions. Examining the elution conditions in this experiment we find that the third band required ca. 1.5 M NaCl. This would be highly uncharacteristic of a unipositive cation. In similar experiments we eluted a violet band on Dowex 50W-X8 with 0.7 M KNO₃, indicating in all probability a dipositive ion, which is most likely a monohistidine complex, $[Cr(L\text{-}his)(H_2O)_3]^{2+}$. We were unable to precipitate the complex for characterization.

The other two fractions reported by Grouhi-Witte had colors appropriate to the two isomers studied here, but the CD spectra of the two fractions were nearly identical. The explanation for this lies in the tendency of the trans(carboxylate) isomer

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to convert to the trans(imidazole) isomer in solution. The reported electronic spectral data are also consistent with a sample which had undergone substantial isomerization.

One-Electron-Reduced Nickel(II)–Macrocyclic Ligand Complexes. Four-Coordinate Nickel(I) Species and Nickel(II)–Ligand Radical Species Which Form Paramagnetic, Five-Coordinate Nickel(I) Adducts

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Mononuclear nickel(II) complexes of tetraaza macrocyclic ligands undergo one-electron reduction to give either nickel(I) species or species containing nickel(II) complexed to a ligand radical. Both reduced species react with carbon monoxidde to give paramagnetic, five-coordinate, nickel(I) carbonyl adducts. The nature of the reduced nickel species and of their carbonyl adducts was examined by EPR and by electronic absorption spectroscopy, which confirm the descriptions as Ni(I) or Ni(II)–ligand radicals. Condensation of 1,4-diaminobutane with 2,3-butanedionemonoxime, followed by reaction with nickel(II) and then BF₃ and, finally, one-electron reduction, gave a complex exhibiting dynamic valence isomerism. At 298 K its EPR spectrum shows signals attributable both to Ni(I) and to a Ni(II)–ligand radical species. On cooling of the solution, the Ni(I) signal disappears with concomitant increase in the Ni(II)–ligand radical signal. Carbon monoxide equilibrium binding constants, measured electrochemically for 11 complexes, ranged from zero to 10⁵ M⁻¹. Carbonyl stretching frequencies for seven five-coordinate complexes in pyridine solution and for two isolated adducts ranged from 1949 to 2020 cm⁻¹. Similarities are suggested between the new nickel complexes and related copper systems.

Introduction

Metal complexes of synthetic tetraaza macrocycles have received a great deal of attention. The kinetic stability toward dissociation that they impose on their complexes apparently contributes to their unusual chemical and electrochemical properties.[1,2] In addition to kinetic stability, certain macrocycles such as some of those employed here lend thermodynamic stability to their metal complexes. Often these macrocyclic ligands stabilize metals in formal oxidation states that normally are not subject to isolation or study in other types of coordination compounds. This affords the opportunity to study the chemical reactivity of uncommon oxidation states in a homeostructural ligand environment and to study the effect of ligand modifications on these chemical properties.

The 14-membered cyclic tetraaza ligands present an excellent opportunity to study the effect of the degree of ligand unsaturation on the chemical reactivity of metal coomplexes.[3,4] Recently, reduced copper complexes, considered as copper(I) species, have been isolated in a macrocyclic ligand environment.[5-8] These complexes show varying affinities for binding π acids as fifth ligands, creating what are best described as "20-electron" Cu(I) complexes.[6,7] These diamagnetic complexes have been regarded as copper(I) compounds for both the four-coordinate and the five-coordinate species.[6-9] In an

effort to better understand the bonding in these unusual d¹⁰ copper complexes, we have examined the analogous four-coordinate, paramagnetic d⁹ nickel complexes, which have been previously studied by Busch et al.[3] In addition, we report here the synthesis and some of the chemical properties of several paramagnetic, presumably five-coordinate, nickel(I) carbonyl complexes,[10] which constitute a new class of coordination compounds.

Results and Discussion

Synthesis, EPR, and Electronic Absorption Spectra. Reduction of cyclic tetraaza–nickel(II) complexes has been shown to give either nickel(I) complexes or metal-stabilized ligand

Table I. EPR Data for Reduced Nickel Complexes in Propylene Carbonate Glass at 100 K

Ni complex	Ar[d]	CO[e]
1[a]	2.002 (20)[b]	$g_{\parallel} = 2.227, g_{\perp} = 2.063\ (10)^c$
2	2.007 (25)[b]	$g_{\parallel} = 2.226, g_{\perp} = 2.065\ (12)^c$
3	2.002 (16)[b]	$g_{\parallel} = 2.225, g_{\perp} = 2.065\ (12)^c$
5[a]	2.000 (23)[b]	$g_{\parallel} = 2.230, g_{\perp} = 2.066$
6[a]	2.008 (35)[b]	$g_{\parallel} = 2.235, g_{\perp} = 2.069\ (12)^c$
7	$g_{\parallel} = 2.253, g_{\perp} = 2.054$	$g_1 = 2.198, g_2 = 2.123, g_3 = 2.012$
8	$g_{\parallel} = 2.235, g_{\perp} = 2.086$	$g_1 = 2.305, g_2 = 2.151, g_3 = 2.056$
9	$g_{\parallel} = 2.220, g_{\perp} = 2.063$	$g_1 = 2.201, g_2 = 2.123, g_3 = 2.018$
10[a]	$g_{\parallel} = 2.190, g_{\perp} = 2.056$	$g_1 = 2.238, g_2 = 2.159, g_3 = 2.066$
11	2.020 (40)[b]	$g_{\parallel} = 2.242, g_{\perp} = 2.068\ (12)^c$

a Generated chemically or electrochemically in situ. *b* Peak-to-peak width (in gauss) of first derivative spectra. *c* Nitrogen superhyperfine (in gauss), where resolvable. *d* Spectra taken in argon-saturated propylene carbonate. *e* Spectra taken in carbon monoxide saturated propylene carbonate.

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