N-Methyl-Substituted Ethylenediamine Complexes of Rhodium(III)[1]

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Abstract: Rhodium(III) complexes of men, udmen, sdmen, tmen, and tetmen have been prepared using a large excess of diamine; only for the preparation of the tetmen complex was it necessary to minimize the presence of water. Substitution of more than one methyl group resulted in the formation of stable bisdiamine *trans*-dichloro complexes even in the presence of excess ligand. The color of the complexes, the infrared and ultraviolet-visible spectra, and X-ray diffraction patterns support the conclusion that the diamines act as normal bidentate ligands in each complex. From the ultraviolet-visible spectral data, the spectrochemical series of ligands for Rh(III) was found to be: udmen > en > sdmen > tmen > tetmen; this order is attributed to increasing steric effects of the methyl groups. The relative thermodynamic stabilities of the complexes are indicated by the correlation found between the nephelauxetic series of ligands and the metal-nitrogen stretching frequencies in the infrared region, giving the following order of decreasing stability: udmen > tetmen > tmen > sdmen > en.

During study of methylation reactions of deprotonated en ligands,[2] it became necessary to undertake direct synthesis of the N-methyl-substituted ethylenediamine complexes of Rh(III).

Recent papers[3-8] report the isolation of such complexes with other transition metals, and it seems clear that, although inductive effects might be expected to increase stability, steric effects of N-methyl substitution seriously hinder complex formation; the extent of hindrance apparently depends to some extent upon the metal ion radius. Bisdiamine complexes of Cu(II)[3-8] and Ni(II)[3] have been prepared with men, udmen, sdmen, and tmen, but attempts to prepare the bis(tetmen) complex of Cu(II) failed[7] even under rigorously controlled conditions; a dimeric hydroxy-bridged complex was isolated instead. With the larger Pd(II), Meek[6] succeeded in preparing bis(sdmen) complexes and $[Pd(tetmen)_2](NO_3)_2$, and Mann and Watson[4] obtained mono(tetmen) complexes of Pd(II), Pt(II), Cu(II), Cd(II), and Ir(IV) but failed to find any complex formation between tetmen and Co(III), Ni(II) and Rh(III).

Tris complexes of these ligands are even less well known, but octahedral complexes of Ni(II) with men, sdmen, and udmen ligands and the men complex of Co(III) have been isolated.[5]

Because of the failure[4] to prepare tetmen complexes of Rh(III) and the lack of information concerning other N-methyl-substituted en complexes, we report here the preparation of Rh(III) complexes of men, udmen, sdmen, tmen, and tetmen together with X-ray diffraction data and ultraviolet-visible and infrared absorption spectra. On the basis of these data, the spectrochemical series of these ligands has been determined, and a correlation between the nephelauxetic series and the metal-nitrogen stretching frequencies has been demonstrated, thus providing evidence for the relative order of thermodynamic stabilities of the complexes.

Experimental Section

Materials. All materials employed in this work were reagent grade and used without further purification.

Synthesis. Each complex was prepared by the addition of a large excess of the appropriate diamine to rhodium(III) chloride trihydrate. The solubility of the complexes in both water and absolute ethanol increased with increasing N-substitution, as did sensitivity to the presence of water. The latter required alterations in the preparative procedure.

A 20-ml aliquot of men was added slowly with constant stirring to 1.0 g (3.81 mmoles) of $RhCl_3 \cdot 3H_2O$. The solution was warmed on a steam bath for 30 min; this resulted in the precipitation of a white solid. After cooling and adding ethanol to effect complete precipitation, the solid was filtered, washed with ethanol, and dried in air. It was then redissolved in the minimum volume of water, and to this solution was added a solution containing a large excess (5 g) of potassium iodide dissolved in the minimum volume of water. A white precipitate formed immediately and, after stirring thoroughly for 30 min, it was filtered, washed with ethanol, and dried *in vacuo*. The yield of crude product was 0.91 g which was recrystallized from warm water, filtered, washed with ethanol, and dried *in vacuo*.

The same procedure with udmen yielded 0.62 g of a bright yellow solid which was recrystallized from warm 50% aqueous ethanol, filtered, washed with ethanol, and dried *in vacuo*. With sdmen the intermediate product, obtained after warming the mixture of diamine and $RhCl_3 \cdot 3H_2O$, was isolated as a bright yellow solid (1.20 g) and recrystallized from warm 50% aqueous ethanol, filtered, washed with ethanol, and dried *in vacuo*. A sample of 0.63 g of the crude product was then treated as above with excess potassium iodide to give a yellow solid. Recrystallization from boiling water yielded 0.32 g of dark orange crystals which were filtered, washed with ethanol, and dried *in vacuo*.

With tmen, the $RhCl_3 \cdot 3H_2O$ was refluxed for 1 hr during which yellow-orange crystals separated. The mixture was transferred to a vessel which allowed filtration in an atmosphere of dry nitrogen and drying *in vacuo*. The yield of crude product was 1.17 g which was recrystallized from a 75% ethanol-ether mixture, filtered under nitrogen, washed with ether, and dried *in vacuo*. A sample of 0.40 g of this solid was dissolved in the minimum volume of water, and excess KI was added. A yellow-orange precipitate formed immediately and, after stirring for 30 min and filtering, 0.23 g was isolated and recrystallized from warm 50% ethanol-water, filtered under nitrogen, washed with ethanol, and dried *in vacuo*.

For preparation of the Rh(III) complex of tetmen, it was found necessary to carry out the reaction under conditions which more rigorously excluded water. A sample of 0.53 g of $RhCl_3 \cdot 3H_2O$

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(1) Abbreviations: en = ethylenediamine; men = N-methylethylenediamine; sdmen = N,N′-dimethylethylenediamine; udmen = N,N-dimethylethylenediamine; tmen = N,N,N′-trimethylethylenediamine; tetmen = N N,N′,N′-tetramethylethylenediamine; dien = diethylenetriamine.

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Table I. Data for Rh(III) Complexes

No.	Complex	Color	Yield, %	Rh, %		C, %		H, %	
				Calcd	Found	Calcd	Found	Calcd	Found
I	$[Rh(men)_3]I_3$	White	49	14.6	14.9	15.4	15.7	4.26	4.47
II	$[Rh(udmen)_2Cl_2]I$	Yellow	34	21.6	21.3	20.1	20.1	4.95	5.15
III	$[Rh(sdmen)_2Cl_2]Cl$	Yellow	66	26.7	27.0	25.0	24.9	6.24	6.41
IV	$[Rh(sdmen)_2Cl_2]I$	Orange	35	21.6	21.6	20.1	19.9	4.95	5.02
V	$[Rh(tmen)_2Cl_2]Cl$	Yellow-orange	68	24.9	25.0	29.1	29.3	6.79	7.03
VI	$[Th(tmen)_2Cl_2]I$	Yellow-orange	48	20.4	20.6	23.8	24.3	5.55	5.63
VII	$[Rh(tetmen)_2Cl_2]Cl$	Yellow-orange	39	23.3	23.4	32.6	32.5	7.25	7.26

Table II. Ultraviolet-Visible Spectral Data for Rh(III) Complexes in Water

Complex	λ_{max}, mμ	ϵ_{max}
$[Rh(en)_3]^{3+}$ [a]	301, 253	210, 190
$[Rh(men)_3]I_3$	312	300
cis-$[Rh(en)_2Cl_2]Cl$ [b]	352, 295	155, 180
trans-$[Rh(en)_2Cl_2]Cl$ [b]	406, 286	75, 130
$[Rh(udmen)_2Cl_2]I$	377, 312	260, 200
$[Rh(sdmen)_2Cl_2]Cl$	418, 300	72, 171
$[Rh(sdmen)_2Cl_2]I$	490, 360, 279[c]	20, 670, 1900
$[Rh(tmen)_2Cl_2]Cl$	444, 322	102, 150
	442, 325[d]	110, 154[d]
$[Rh(tmen)_2Cl_2]I$	444, 322	116, 212
$[Rh(tetmen)_2Cl_2]Cl$	460, 359, 330[c]	63, 157, 172
	454, 362, 317[c]	65, 147, 187[d]

[a] Reference 15. [b] Reference 16. [c] Shoulder. [d] Absolute ethanol.

was refluxed with constant stirring in a solution containing 10 ml of tetmen, 25 ml of ether, and 10 ml of absolute ethanol for 3 hr. The orange-yellow crystals which precipitated were filtered under nitrogen and dried *in vacuo*. The yield of crude product was 0.23 g which was recrystallized from a warm 80% ether–ethanol mixture as an orange-yellow solid, filtered under nitrogen, washed with ether, and dried *in vacuo*. The product was hygroscopic and was therefore stored and sampled in a drybox.

Analytical and other data relating to these complexes are listed in Table I.

Spectral Measurements. The ultraviolet–visible absorption spectra of the complexes in either water or absolute ethanol were obtained with a Cary Model 14 recording spectrophotometer using matched 1-cm quartz cells. The data are given in Table II.

The infrared absorption spectra were recorded with a Beckman IR-7 spectrophotometer equipped with NaCl and CsI optics. The complexes were studied as Nujol mulls in the region 200–600 cm^{-1} and as KBr disks in the range 600–4000 cm^{-1}. The band positions and intensities are listed in Table III.

X-Ray Data. X-Ray diffraction patterns were obtained with Cu Kα radiation (Ni filter) at 35 kv and 15 ma and exposure times of 12–15 hr; relative intensities were estimated visually. The data are recorded in Table IV.

Results and Discussion

From the elemental analyses in Table I it is clear that, under the experimental conditions used, the bis(diamine) complexes of Rh(III) were formed in all cases except that of men where the tris complex was obtained. This is true despite the presence of a large excess of ligand, so that with N-substitution of methyl groups exceeding one per diamine molecule the formation of the tris complexes of Rh(III) is apparently inhibited. This effect is in agreement with earlier observations[9–12] that, although basicity is increased, N-alkyl substitution in en decreases complex stability owing to steric interactions. That the bis(tetmen) complex forms at all is surprising since the only similar complex previously isolated is that of Pd(II)[6] with its larger ion radius, while only very few N-methyl-substituted en complexes of d^6 octahedral symmetry have been reported.[4,13,14]

Evidence that the four nitrogen atoms are in fact coordinated to the metal in $[Rh(tetmen)_2Cl_2]Cl$ (VII) is provided by the infrared spectrum. Table III shows that the bands at 2750 and 2800 cm^{-1} in the spectrum of tetmen are not present in that of the Rh(III) complex. The shift of these bands has been attributed[4] to chelation of the donor nitrogen atoms.

The ultraviolet-visible spectral data are listed in Table II together with the previously reported[15] data for $[Rh(en)_3]^{3+}$ and *cis*- and *trans*-$[Rh(en)_2Cl_2]Cl$.[16] The spectra exhibit the expected characteristics[15] of complexes with 6d electrons and a singlet ground state in an octahedral field. The change in color of the solids from yellow to orange is in agreement with the observed spectral shifts to longer wavelengths with increasing N-substitution. For two of the complexes, measurements were made in both absolute ethanol and water to establish stability in aqueous solution.

There were no significant differences between the spectra in ethanol and water when measured immediately after preparing the solutions. However, a slow change with time did occur in the aqueous solutions; this was most noticeable for the sdmen and udmen species and amounted to approximately 5% in the ϵ values over 24 hr but to only about 1% in the ϵ values for the tetmen complex.

These changes can apparently be attributed to rearrangement of geometrical configuration in neutral aqueous solution. Two complexes of sdmen were prepared: the bright yellow chloride from aqueous ethanol and the dark orange iodide from hot water. The infrared spectra of the two (Table III) are virtually identical while the visible absorption maxima given in Table II are quite different and characteristic of *cis–trans* isomers. The empirical rule of Shimura,[17] *viz.*, $\nu_{max}(cis) - \nu_{max}(trans) > 0$, allows the assignment of the *cis* configuration to the iodide, and its higher ϵ values confirm this so long as the band at 490 mμ is considered a spin-forbidden transition as discussed below. The change in the aqueous solution spectrum of this iodide was found to be much faster than for any of the other complexes, and after 2 days the absorption maxima had decreased in intensity by about 80% with the appearance of a band at 418 mμ characteristic of the

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Table III. Infrared Absorption Bands (cm^{-1}) of Rh(III) Complexes

I	II	III	IV	V	VI	VII
3155 vs	3260 vs	3150 vs	3150 vs	3088 s	3115 s	3045 s
3095 vs	3185 vs	3015 s	3013 ms	3010 sh	3040 sh	3025 s
3060 vs	3100 vs	2998 ms	2990 s	2950 s	3005 m	3005 m
2890 sh	2925 ms	2950 ms	2945 ms	2880 sh	2940 s	2935 s
2855 s	2850 sh	2890 m	2890 m	1480 sh	2870 sh	2840 sh
1580 s	2810 sh	2805 sh	2802 sh	1471 s	1480 sh	2660 s
1568 s	2340 vw	1478 sh	1475 sh	1456 s	1470 s	2580 sh
1472 s	1571 s	1466 sh	1460 sh	1429 sh	1452 s	2520 sh
1454 s	1478 s	1449 s	1446 s	1407 m	1430 sh	2465 m
1432 sh	1463 s	1429 s	1434 sh	1388 sh	1405 m	1482 s
1422 m	1455 sh	1413 s	1427 s	1349 m	1388 sh	1473 vs
1415 m	1430 sh	1373 w	1411 s	1303 m	1349 m	1463 sh
1378 w	1405 s	1341 w	1370 w	1293 m	1293 sh	1425 s
1392 w	1397 m	1289 ms	1341 w	1285 m	1285 m	1407 s
1358 w	1362 m	1283 m	1286 m	1225 m	1225 m	1353 m
1346 w	1313 m	1233 m	1280 ms	1188 mw	1188 w	1296 sh
1316 m	1294 m	1193 m	1230 m	1164 mw	1163 w	1278 s
1296 m	1244 m	1165 m	1190 w	1116 w	1116 w	1236 m
1287 sh	1202 ms	1147 m	1165 m	1087 sh	1097 sh	1199 s
1275 w	1165 s	1084 ms	1143 w	1079 s	1079 s	1175 w
1269 sh	1119 s	1055 vs	1080 ms	1055 vs	1055 s	1158 w
1225 m	1102 sh	1031 sh	1056 vs	1036 m	1040 s	1121 m
1201 m	1087 vw	1005 sh	1048 sh	1022 sh	1022 sh	1057 m
1155 ms	1062 s	991 sh	1031 sh	998 sh	998 s	1100 vw
1130 m	1035 s	980 s	990 sh	985 s	985 s	1040 m
1117 m	994 sh	860 s	975 s	939 s	939 s	998 s
1082 m	981 s	825 m	860 s	854 s	854 s	990 sh
1063 s	941 s	611 m	825 m	786 s	786 s	951 s
1054 ms	895 s	498 s	615 m	595 w	593 w	917 w
1030 s	781 s	474 m	505 s	518 m	515 m	852 w
1101 s	743 w	411 m	475 m	490 sh	497 sh	801 vs
995 sh	575 m	343 s	410 m	467 vw	489 w	785 sh
985 w	531 ms	327 s	343 s	420 m	460 vw	774 s
957 m	481 vw	313 s	327 s	410 sh	421 sh	603 w
893 m	449 vw	274 s	310 s	347 s	412 w	537 m
880 w	416 vw		275 s	295 w	348 s	517 m
843 m	340 ms			262 m	295 w	494 sh
837 sh	306 sh				258 m	416 w
322 m	295 s					361 m
765 vw	280 sh					276 m
740 w						
720 sh						
710 w						
586 ms						
574 ms						
574 ms						
556 ms						
502 m						
490 sh						
480 m						
460 w						
420 sh						
415 w						
356 ms						
325 w						
305 m						
263 w						

Table IV. X-Ray Diffraction Data[a]

I		II		III		IV		V		VI		VII	
d, A	I/I_0	d, A	I/I_0	d, A	I/I_0	d, A	I/I_0	d, A	I/I_0	d, A	I/I_0	d, A	I/I_0
5.66	0.6	8.15	0.3	7.46	0.1	7.56	0.3	9.93	0.6	8.58	0.4	10.97	0.7
4.87	0.3	6.83	0.7	6.80	1.0[b]	7.08	0.3	7.32	1.0	7.43	0.6	8.75	0.5
4.29	1.0	6.28	0.9	6.41	1.0[b]	6.53	1.0	6.32	1.0	6.30	1.0	7.46	0.3
4.15	0.2	5.40	1.0	5.24	0.7	5.17	0.1	5.42	0.6	5.84	0.8	7.08	1.0[b]
4.02	0.1	4.96	0.8	4.25	0.6	4.41	0.8	4.78	0.7	5.53	0.8	6.60	1.0[b]
3.74	0.2	4.68	0.7	4.05	0.6	4.23	0.4	4.24	0.4	4.22	0.5	6.04	0.8
3.48	0.8	3.82	0.7	3.39	0.5	4.08	0.3	3.60	0.3	3.80	0.7	5.18	0.6
3.24	0.6	3.61	0.8	3.26	0.6	3.58	0.5	3.32	0.5	3.62	0.6	4.63	0.3
2.99	0.1	3.21	0.4	2.63	0.8	3.35	0.7	2.91	0.8	3.40	0.6	4.45	0.3
2.44	0.1	3.11	0.4	2.48	0.4	2.68	0.5	2.71	0.8	3.03	0.7	3.39	0.3
		3.02	0.4	2.42	0.3	2.63	0.5	2.59	0.4	2.83	0.6	3.15	0.3
												2.86	0.5

[a] Less intense lines not included. [b] Broad lines.

trans chloride. A similar change has been observed[16] in dilute aqueous solutions of $[Rh(en)_2I_2]^+$ and attributed to *cis–trans* isomerization rather than aquation. Our data are therefore considered to provide evidence that the *trans* configuration is preferred in both the solid state and in dilute solution and that aquation is not important.

If it is concluded that all the bis complexes are *trans* isomers except $[Rh(sdmen)_2Cl_2]I$, the spectrochemical series of ligands for Rh(III) may be deduced from the position of the long-wavelength band in the visible region. In general, it is found[18] that, as the thermodynamic stability of complexes decreases, the absorption maximum is shifted to a lower energy, on the basis of which the order of decreasing stability is expected to be equivalent to the spectrochemical series, *i.e.*, udmen > en > sdmen > tmen > tetmen.

However, with regard to relative stabilities, the metal–nitrogen stretching modes in the infrared region are of interest, and these data are given in Table V. Such modes have been assigned for $[Rh(en)_3]I_3$,[19] $[Pd(en)_2]I_2$,[20] $[Pt(en)_2]I_2$,[20] and $Pd(dien)Cl]Cl$[21] in the interval 500–600 cm^{-1}. The bands in similar positions in the spectra of N-methyl-substituted en complexes have therefore been assigned as the Rh–N stretching modes.

Table V. Metal–Nitrogen Stretching Modes for Rh(III) Complexes

Complex	ν(Rh–N), cm^{-1}
$[Rh(en)_3]I_3$[a]	570 w, 558 w
$[Rh(men)_3]I_3$	586 m, 574 m, 556 m, 502 m
$[Rh(udmen)_2Cl_2]I$	575 m, 531 s
$[Rh(sdmen)_2Cl_2]Cl$	498 s, 474 m
$[Rh(sdmen)_2Cl_2]I$	505 s, 475 m
$[Rh(tmen)_2Cl_2]Cl$	518 m, 490 sh
$[Rh(tmen)_2Cl_2]I$	515 m, 497 sh
$[Rh(tetmen)_2Cl_2]Cl$	537 m, 517 m

[a] Reference 19.

The data indicate a trend in ν(Rh–N) to lower energies in both the antisymmetric and symmetric stretching modes as N-substitution is increased to two methyl groups, but surprisingly with further substitution ν(Rh–N) increases. The order of decreasing Rh–N bond energies of the bis(diamine) complexes must therefore be udmen > tetmen > tmen > sdmen and is significantly different from the spectrochemical series. en is not included because ν(Rh–N) for *trans*-$[Rh(en)_2Cl_2]Cl$ has not been reported.

A correlation can, however, be made with the nephelauxetic series of ligands which is characterized by the parameters of interelectronic repulsion in a given complex. By methods discussed by Jørgensen,[22] the order of ligands in this series is deduced from the two broad, spin-allowed transitions in the ultraviolet–visible spectra, udmen > tetmen > tmen > sdmen > en, listed in order of decreasing nephelauxetic effect. The good agreement with the order of the metal–nitrogen bond energies is evident, and the position of the tertiary amines before the secondary and primary is consistent with the more diffuse electron density about nitrogen in the tertiary amines resulting in the greater nephelauxetic effect.

The Tanabe–Sugano diagram for the Rh(III) complexes of the 4d^6 system should resemble that of Co(III) and, in octahedral field, two spin-allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, are predicted as well as two singlet–triplet transitions, $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$. For the *trans*-dichloro complexes the effective symmetry is D_{4h}, although the actual symmetry can be no higher than D_{2h}, and the ground state remains $^1A_{1g}$ as in strict O_h symmetry. The excited singlet states are, however, expected to be split and $^1T_{1g}$ becomes $^1A_{2g} + {}^1E_g$ and $^1T_{2g}$ becomes $^1B_{2g} + {}^1E_g$. In practice, the $^1T_{1g}$ splitting has been observed in numerous cases, *e.g.*, *trans*-$[Co(en)_2Cl_2]Cl$,[23] but the $^1T_{2g}$ splitting is unknown. For all these Rh(III) complexes, two d–d transitions occurred but no splitting was obvious, the energy difference between the $^1A_{2g}$ and ^1E_g states apparently being too small. The two bands are therefore assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. The only possible singlet–triplet transition is the band at 490 mμ in the spectrum of *cis*-$[Rh(sdmen)_2Cl_2]I$.

The wavenumber of the low-energy spin-allowed band determines the position of the complex in the spectrochemical series, but it has been made clear[5] that the band energy is associated with both steric and inductive effects. Although N-methylation increases the electron density at the donor nitrogen atom, which might be expected[18] to result in an increase in the transition energies, the observed shift is to lower energies. The steric effect of the methyl groups is therefore an important factor in the determination of the spectrochemical series. This effect is also indicated by the band intensities. The ratio of the molar extinction coefficient of the long-wavelength band to that of the short-wavelength band (ϵ_I/ϵ_{II}) is seen to decrease with increasing substitution which is attributed to distortions from the expected D_{4h} tetragonal symmetry. The increase in ϵ_{II} with respect to ϵ_I is associated with enhanced probability of the electronic transitions to the $^1T_{2g}$ state as the distortion progresses.

It is this distortion which may account to some extent for the differences between the spectrochemical series and the order found for both the Rh–N stretching frequencies and the nephelauxetic series where the complexes containing the tertiary amino groups are placed ahead of those with primary or secondary groups. This latter order is of course the one expected if only inductive effects are considered. Since considerable steric interactions are indicated by the ultraviolet–visible spectra, we conclude that the inductive and steric properties are additive toward increased metal ion–ligand interaction when the steric distortion becomes large enough. The approach of a metal ion of sufficient radius and high charge toward a diamine molecule can apparently bring about distortion of a tertiary amino group in such a way that the increased electron density at the nitrogen atom is allowed to function normally and produce an increase in the metal–nitrogen bond energy.

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Other factors may also be important since both acid dissociation and metal complex stability constant measurements for amines in aqueous solution are known[24] to be complicated by solvation terms, ion-pair association, and entropy effects. The acid dissociation constants reported for udmen[11] and en, sdmen, and tetmen[12] are a net reflection of these effects and give the following order of increasing basicity: $R_2NH > RNH_2 > R_3N > NH_3$. Similarly the formation constants measured for Cu(II) and Ni(II) diamine complexes[9-12] are influenced by these competitive reactions as well as by the steric effects of increasing N-methyl substitution. It has further been shown[24] that, although primary aliphatic amine complexes of Ni(II) dissociate readily in water, the amines occupy a higher position than water in the spectrochemical series. Accordingly, the instability of these complexes in water cannot be attributed to the relative strength of the metal ion–ligand interaction of water and the amines.

However, any factor that increases metal–nitrogen bond strength would be expected to influence both ν(Rh–N) and the nephelauxetic series, the latter of which is considered[5,22] to represent closely the tendency toward covalent bonding and as a result is primarily dependent on inductive and polarization factors. It is also known[25] that the nephelauxetic series often more closely resembles the order of thermodynamic stability constants than does the spectrochemical series, and a correlation has previously been found[26] between the metal–nitrogen stretching frequencies and stability constants of a number of en complexes. The agreement in the order of the ligands in the ν(Rh–N) series and the nephelauxetic series is therefore consistent with previously observed trends and is a good indication that the thermodynamic stabilities would follow the same order. The data, therefore, provide evidence that the complexes are examples of systems containing tertiary amino groups more stable thermodynamically than those with primary or secondary amines.

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Complexes of Chromium(III) with Some N-Substituted Ethylenediaminetriacetic Acids[1]

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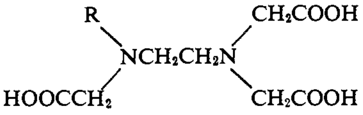
Abstract: A potentiometric, polarographic, and spectrophotometric study of the complexes of Cr(III) with N-(2-hydroxyethyl)ethylenediaminetriacetic acid, N-(2-hydroxycyclohexyl)ethylenediaminetriacetic acid, and N-phenethylethylenediaminetriacetic acid has been carried out. Several equilibrium and kinetic parameters of these systems have been determined. The mechanisms of the electrode reductions are discussed.

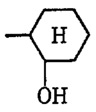
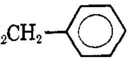
We have studied complexes of Cr(III) with ligands of the type



We will use the designations in Chart I for these ligands to emphasize the number of replaceable hydrogens. The Cr(III) complex of H_3QCOOH (more commonly known as EDTA) has been studied previously by several authors.[2-4] We have performed some additional experiments on this system to compare it with the triacetic acid systems.

Previous work on this Cr(III) complex of EDTA has shown that one coordination position is occupied by a water molecule and that the complex has interesting acid–base and redox chemistry.

Chart I

R	Designation
$-CH_2CH_2OH$	H_3TOH
	H_3XOH
$-CH_2CH_2-$ 	H_3Z
$-CH_2COOH$	H_3QCOOH

Experimental Section

Analytical grade reagents and water triple-distilled from quartz were employed. The ligands were received in purified form, most having been used in a previous study.[5] Chromium(III)–ligand

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