TABLE V

MEASURED MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS

Compound	Temp, °C	$10^6\chi_m'$, cgsu	μ_{eff}, BM	θ, °K
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	297	1226	1.71	2
	195	1885	1.72	
	77	4747	1.72	
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	297	1252	1.73	4
	195	1915	1.74	
	77	4956	1.75	
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$	297	1067	1.60	−1
	195	1605	1.59	
	77	4080	1.60	
$[(C_3H_7)_4N]MoOCl_4$	297	1216	1.71	2
	195	1837	1.70	
	77	4628	1.70	
$[(C_4H_9)_4N]MoOCl_4$	297	1224	1.72	4
	195	1912	1.73	
	77	4841	1.73	

for the previous different product observation. Properties of $[(C_2H_5)_4N]WBr_6$ agreed with those previously reported.[18]

The release of an alkyl group by monoalkoxide complexes tends to confirm the expected greater stability of a complete double bond in M=O compared to the partial π-bond character for oxygen in M—O—R. The far-infrared data (Table I) also probably indicate that the bond *trans* to the metal–oxygen is weakened. The low-frequency M–X band is probably the M–X stretch *trans* to the alkoxide group. The greater instability of the molybdenum compound compared to the tungsten complex ought to be due to better overlap of the oxygen p orbitals with the t_{2g} orbitals of the molybdenum in forming Mo–O. Thus, a weaker metal–halogen bond *trans* to the alkoxide group is the result. Although the frequency of the metal–oxygen bond *trans* to the alkoxide increases as the size of the alkyl group increases, the rate of alkyl halide evolution decreases.[7] It is conceivable that the rearrangement in the solid state is hampered by the larger alkyl group.

The elimination of alkyl halide is viewed as a concerted process that involves an axial chloride from one ion with the alkyl group from a neighbor. Evidence points to an intermolecular process since the rate of alkyl halide evolution decreased as the size of the cation increased. The driving force is the formation of the more stable metal–oxygen double bond.

Acknowledgment.—This work has been supported by Grant GP-7088X from the National Science Foundation.

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[18] B. J. Brisdon and R. A. Walton, *J. Chem. Soc.*, 2274 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Absorption and Circular Dichroic Spectral Studies of Europium(III) Complexes with Sugar Acids and Amino Acids, with Remarks on "Hypersensitivity"[1]

BY LEONARD I. KATZIN

Received January 20, 1969

Chelate complexes of Eu(III) with sugar acids, both in the acid and neutral pH ranges, are demonstrated. Complexing takes place through the carboxylate group and the γ-hydroxyl, revealed by the CD relations of the gluconic and galactonic acid complexes. In addition to chelate complexes of the α-amino acids in the neutral to alkaline pH range, monodentate complexes with the zwitterionic form are demonstrated. Besides the known "hypersensitive" behavior of the $^7F_0 \rightarrow {}^5D_2$ transition in the absorption spectrum, hypersensitivity is also indicated for the $^7F_0 \rightarrow {}^5D_0$ and $^7F_1 \rightarrow {}^5D_1$ transitions and perhaps in others which share the relation $|\Delta J| = 0, 2$. A requirement seems to be binding of an anion, which may include reduction of symmetry. Some potentially revealing characteristics of the CD spectra are pointed out.

The absorption spectra of the trivalent rare earth ions are relatively unaffected by varied chemical environments and ligands, certainly in comparison with the more familiar 3d series of transition elements. This is commonly attributed to the "buried" or shielded nature of the 4f orbitals, presumably lying at shorter radii than others in the atomic complement. For the tripositive ions retaining three or more f electrons (or equivalent holes), however, one or a few transitions out of the whole spectrum show marked enhancement of intensity when water in the coordination sphere is replaced by certain other ligands. These transitions have received the designation "hypersensitive," and several theoretical suggestions have been offered for the orgin of the phenomenon.[2–4]

We have shown that chelating ligands (hydroxy acids and amino acids) markedly alter rare earth ab-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. K. Jørgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).

[3] B. R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).

[4] W. T. Carnall, P. R. Fields, and K. Rajnak, Report No. ANL-7358, Argonne National Laboratory, Argonne, Ill., March 1968; W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965); W. T. Carnall, P. R. Fields, and K. Rajnak, *ibid.*, **49**, 4412, 4450 (1968).

sorption spectra.[5-7] It has further been shown that circular dichroism (CD) observations[6,7] on systems with a ligand that is optically active show marked effects and unique information, both as regards the species in solution and as to certain spectral details of the central metal ion. The most detailed investigation was made for Pr(III) as the central ion.[6,7] This has a $^3H_4$ ground state normally, with two f electrons, and spectral effects attributable to splittings in the ground state were found. We have now extended the observations to Eu(III). The ground state is $^7F_0$, though higher *J* levels of the ^7F group are also occupied and contribute to the spectrum. With f^6, Eu(III) shows recognized hypersensitivity in the $^7F_0 \rightarrow {}^5D_2$ transition. Our studies have revealed some additional features, which will be reported.

Experimental Procedures

Stock $EuCl_3$ solution (*ca.* 1.3 *M*) was made by dissolving 99.9% pure Eu_2O_3 in HCl. Reagent organic acid was dissolved, an aliquot of the $EuCl_3$ was added to the solution, and pH and volume were adjusted as desired. Solutions measured were *ca.* 0.2–0.25 *M*. Adjustments of pH were done with 5 *M* NaOH or 9 *M* NH_3 for the hydroxy acids, and with the ammonia for the amino acids. Spectral observations were made in 50- and 100-mm path length cells, with the JASCO ORD/UV/CD-5 as previously indicated.[6,7] Structural formulas for the sugar acids are given in ref 6.

Results

Our spectral observations are limited to the approximate span 625–360 nm (16,000–28,000 cm^{-1}). The transition intensities seen below 25,000 cm^{-1} (*cf.* Carnall, *et al.*[4]) are exceptionally weak, the strongest being about 0.1 molar absorbancy unit. The transitions above 25,000 cm^{-1} are considerably more intense, being generally several times this maximum value. All of the transitions in the 16,000–25,000-cm^{-1} region are to $^5D_{0-3}$ upper levels.[4] The main transitions of the 25,000–28,000-cm^{-1} region are to ^5L and ^5G levels, though the $^5D_4$ levels are also seen and will be referred to. A representative spectrum for $EuCl_3$ in water is shown in Figure 1a.

Transitions may originate in one of several low-lying ^7F levels. For brevity, a transition from the ground $^7F_0$ level will be designated simply by the symbol of its upper state, *e.g.*, $^5D_1$. If the lower level is the $^7F_1$ state, the symbol will be enclosed in parentheses, as ($^5D_1$), and for origin in the $^7F_2$ state, double parentheses will be used, as (($^5D_1$)). All assignments are those of Carnall, *et al.*[4]

The highest peak in the aqueous spectrum of the 16,000–25,000-cm^{-1} region is the $^5D_1$ transition (molar absorbancy, 0.1), and the next highest is that of $^5D_2$. Both of these transitions, as well as the much more intense $^5D_4$ near 27,700 cm^{-1}, are very sharp. In what follows, the $^5D_1$ peak will be used as an internal reference, since its intensity and shape seem effectively unaltered by the chemical influences which change other parts of the spectrum.

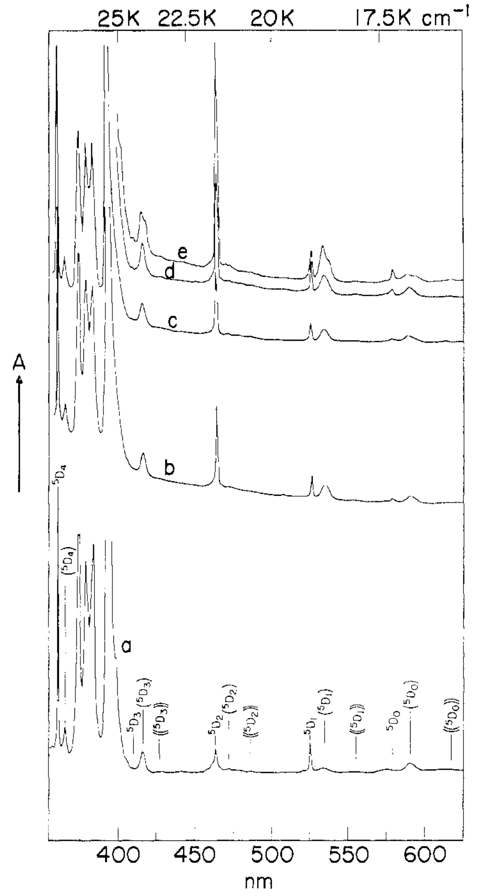

Figure 1.—Absorption spectra of Eu(III) solutions: (a) $EuCl_3$ in water, with upper levels from the ground state $^5F_0$, from ($^5F_1$), and from (($^5F_2$)) indicated; (b) with alanine, pH 5; (c) with alanine, pH 7; (d) with galactonic acid, pH 4; (e) with galactonate, pH 6.

It was deduced from the prior studies[6,7] with Pr(III) that gluconate and galactonate anions, in the pH range 3–5, will form a chelate with a rare earth ion in which the ligand is singly charged. With Eu(III), the most striking spectral effect of this chelation is an increase in the intensity of the $^5D_2$ transition by a factor of 9–10 (or to about 8 times the reference $^5D_1$) (Figure 1). This is, in fact, the recognized "hypersensitive" transition for Eu(III), and the increase makes it comparable in intensity with the transitions above 25,000 cm^{-1}.

However, this is not the only transition which shows a very large change. The others seem less obvious primarily because they do not achieve such high absorbancies, but they start from lower initial intensities. The ($^5D_1$) peak at 18,700 cm^{-1}, which is very weak relative to the $^5D_1$ in aqueous solution and is inherently broader, becomes about as intense as the reference. The $^5D_0$ transition at about 17,300 cm^{-1}, vanishingly weak in the aqueous spectrum (presumably because of $J = 0 \rightarrow J = 0$), becomes perhaps 0.3 times the intensity of the reference $^5D_1$. The broad (($^5D_2$)) is very weak in the aqueous spectrum and still not strong in the complex, but the impression is that it, too, has increased.

The zwitterionic amino acids also possess an ionized

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[5] L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).
[6] L. I. Katzin, *Inorg. Chem.*, **7**, 1183 (1968).
[7] L. I. Katzin and E. Gulyas, *ibid.*, **7**, 2442 (1968).

carboxyl and, in spite of the positive $-NH_3^+$ group on the α-carbon, must form a monodentate complex with the Eu(III), since similar spectral changes are produced, but with only half the intensity (*i.e.*, $I(^5D_2)/I(^5D_1) \approx 4$). The complexing is verified by the fact that a definite, though rather weak, circular dichroism appears in conjunction with the $^5D_1$ transition, and indications of dichroism appear also at other points of the spectrum. Serine, with its hydroxyl group, appears to show more CD effect than alanine or asparagine.

Gluconate, with strong complexing action, produces a markedly stronger circular dichroism, and again the most intense dichroism is associated with the $^5D_1$ transition (Figure 2). The CD effect of galactonate is weaker below 25,000 cm^{-1}, and the sign of the CD at the $^5D_1$ is opposite to that for the gluconate complex (and to that of the amino acids, which have the gluconate sign). Other CD transitions below 25,000 cm^{-1} are weak, but the impression is gained that the signs for the galactonate are different than for the gluconate. The latter shows less CD complexity at the $(^5D_0)$ than does the galactonate, which has both positive and negative components.

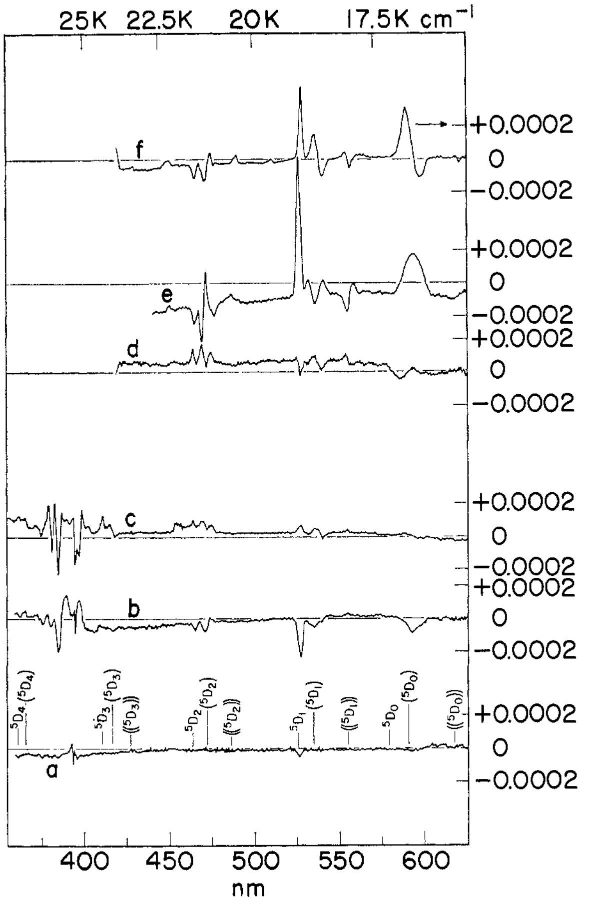

Figure 2.—Circular dichroism spectra of Eu(III) solutions: (a) with alanine, pH 5; (b) with gluconate, pH 5–6; (c) with galactonate, pH 4; (d) with galactonate, pH 6; (e) with gluconate, pH 6–7 (zero displaced); (f) with alanine, pH 7. Optical transition indications are as in Figure 1.

Above 25,000 cm^{-1} the complexes with the amino acids show possibly a weak effect in the most intense absorption, at about 394 nm. Gluconic acid shows a noticeable complex dichroism, particularly in the 385–390-nm region (Figure 3), and has a small positive dichroism at the 361-nm $^5D_4$ absorption. The galactonic acid complex has relatively the strongest CD above 25,000 cm^{-1}, though the effect at the sensitive $^5D_1$ and elsewhere below 25,000 cm^{-1} seems less than that for gluconic acid. A very small dichroism at the $^5D_4$ absorption is negative, opposite in sign to that for gluconic acid.

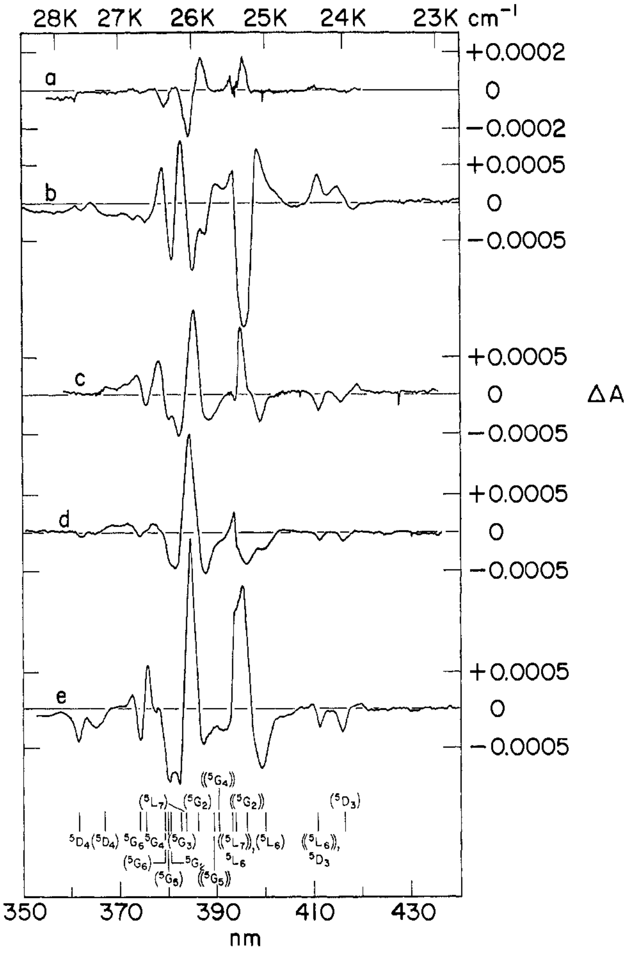

Figure 3.—Circular dichroism spectra of Eu(III) solutions in the 23,000–28,000-cm^{-1} region: (a) with galactonate, pH 4; (b) same, pH 5–6; (c) with gluconate, pH 5–6; (d) with serine, pH 6; (e) with alanine, pH 6–7. Optical transitions are as indicated previously.

In this spectral region, though there are no striking absorption changes comparable with those noted at longer wavelengths, there seems to be a broadening of the 394-nm absorption peak to the long-wavelength side, and there is a small change in the intensity relations of the approximately 379- and 384-nm absorption maxima. In water, the second is more intense, whereas in the "acid" sugar acid complexes they are about equal in height. For the zwitterionic amino acid complexes, the intensity relations of these peaks are as in the water spectrum.

As NaOH or NH_3 is added to the europium(III)-

gluconic acid system, an obvious buffer resistance is met in the region of pH 5–6, which is complete near pH 6. This chemical reaction is accompained by a sharp change in the CD patterns (Figures 2, 3). The region above 24,000 cm^{-1}, which showed some weak CD structure before, now reveals a quite intense and highly structured series of CD extrema, the most intense of which fall in the 384- and 394-nm absorption peaks. Both positive and negative transitions are seen. In the lower frequency region 16,000–24,000 cm^{-1} there is also marked change and intensification of the CD, but the contrast is less startling than in the higher frequency region. In this lower frequency region there is more complexity than for the "acid" complex, both positive and negative components being revealed. Some weak transitions, such as (($^5D_1$)), which hardly register on the absorption spectrum, show a rather strong CD structure. Further, transitions which had significant CD effects in the acid complex region (*e.g.*, $^5D_1$ and ($^5D_0$)) also show stronger CD transitions now, but with the sign inverted from that in the low-pH complex.

The pattern of chemical effect in the galactonate case is basically the same, but there are some complications introduced by the slow hydrolysis of the reagent lactone. The transition from "acid" to "neutral" complex seems to take place at a little lower pH than with gluconic acid and may be largely complete at pH 5. As with the gluconate complex, large CD effects accompany the change. In the cases of a number of isolated transitions—*e.g.*, $^5D_1$, ($^5D_3$), [$^5D_3$, or ($^5L_6$)]—the signs of the CD are clearly inverted between the galactonate and gluconate complexes. In others—*e.g.*, ($^5D_0$) and the complex 390–400-nm region—there are splitting differences or variations and a number of relative intensity differences—*cf.* ($^5D_1$), $^5D_4$, and ($^5D_4$), for example.

The complexes with alanine and serine have a buffer region to NH_3 addition at pH 6–7 (asparagine is not able to inhibit Eu(III) precipitation), and as with the hydroxy acids, a strong, structured CD appears (Figures 2, 3). Where they can be compared, at the $^5D_1$, $^5D_2$, ($^5D_3$), ($^5D_4$), and $^5D_4$ transitions, the amino acid complexes show the same CD signs as the gluconate complex and are opposite in sign to the galactonate complex. There are differences in intensities and structuring at various places in the spectrum not only between the amino acid and sugar acid complexes, but between the alanine and serine complexes, where the β-hydroxyl group of the serine is an undoubted influence.

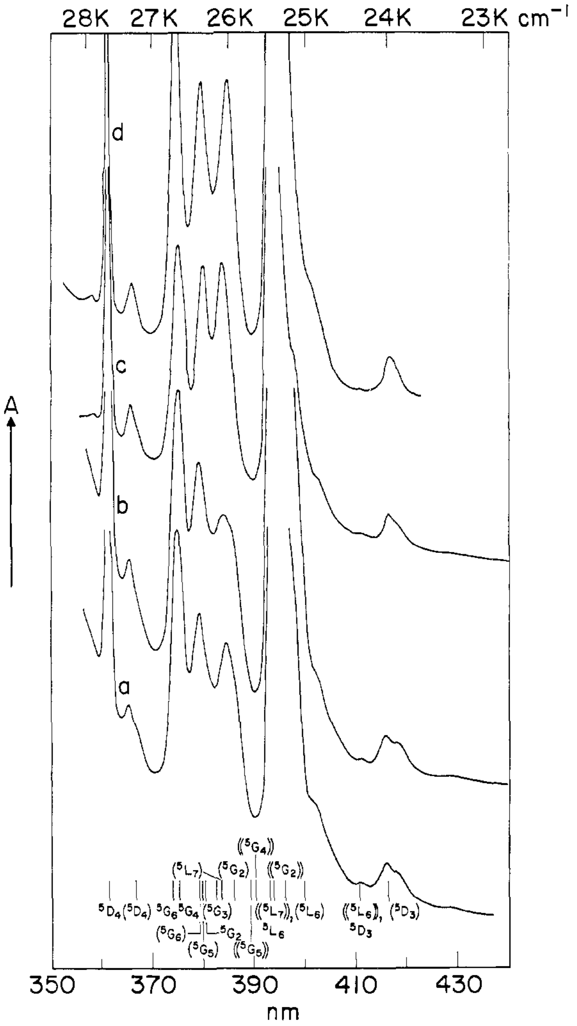

Figure 4.—Absorption spectra of Eu(III) solutions in the 23,000–28,000-cm^{-1} region: (a) with gluconate, pH 5–6; (b) with galactonate, pH 5–6; (c) with alanine, pH 6–7; (d) with galactonate, pH 4. Optical transitions are as indicated previously.

For the sugar acid complexes, the chemical change induces two definite alterations in the absorption spectrum (Figure 4). The ($^5D_3$) develops a definite splitting, with component frequencies both above and below the original extremum. Also, the 379-nm peak is now definitely higher than the 384-nm one, which has decreased in height, with a definite broadening to an incipient shoulder on the low-energy side. The absorption spectra of the chelated amino acid complexes of Eu(III) are now with difficulty distinguishable from those for the "acid" complexes of the hydroxy acids. The essential distinction is that the hypersensitive transitions still are in the lower ratio of intensity to the marker $^5D_1$; the 379- and 384-nm absorption extrema are now equal in intensity, as with "acid" sugar acid complexes.

If the europium(III)–sugar acid systems are made definitely alkaline, *e.g.*, pH 8–9, there is little effect that can be identified on the absorption spectrum, but changes in the CD are readily observed. One such change is a sharp drop in the intensity of the CD transitions above 24,000 cm^{-1} to something like 0.2 of their value in the "neutral" complex. Some indications of splitting shifts are also seen. In the lower frequency region there is a tendency for increased complexity of the CD, with frequent splittings into positive and negative components. This is striking with the ($^5D_0$) and particularly with the $^5D_1$ transitions, which were previously uniform in sign. There is also indication of a relatively strong, and probably paired, CD arising for the $^5D_2$ transition, for which a CD distinguishable from that for the ($^5D_2$) components could not be clearly identified either in the "acid" or in the "neutral" complex. Some slow changes with time seemed indicated, with a possible mixture of species, in the alkaline medium.

Discussion

Chelate complexes of Pr(III) produce splittings of the metal ion ground state ($J = 4$), and for an upper state with $J = 0$ (*i.e.*, $^3P_0$) transitions from more than one of the ground-state levels are seen.[5-7] With Eu(III), for which $J = 0$ in the *ground* state, all of the upper levels $^5D_{0-4}$ show relatively sharp, single transitions from the ground state. This suggests that these upper states are not split even when $J \neq 0$. This is different from the $^3P_{1,2}$ upper states for Pr(III), where spectra which have similar ground-state splittings vary in the transitions to the upper states, and there may be variations between the upper states in the same spectrum.

The apparently hypersensitive transitions, $^5D_0$, ($^5D_1$), $^5D_2$, and (probably) ($^5D_3$), all conform to the rule that $|\Delta J| \leq 2$. (In fact, the rule seems here, and rather generally, to be $|\Delta J| = 0, 2$, as the only $|\Delta J| = 1$ transition so far claimed to be hypersensitive is the $^6H_{5/2} \rightarrow {}^6F_{3/2}$ of Sm(III), in molten lithium nitrate–potassium nitrate medium.[8]) The degrees of hypersensitive intensification seem linked, if not actually the same, in these several transitions in a given complex, suggesting that the same mechanism is operating. All of these transitions have significant enough values of the integral $U(2)$ to tabulate,[3,9] except for $^5D_0$, which is forbidden. ($^5D_1$ is also electronically forbidden but is magnetically allowed.)

Zwitterionic alanine must obviously complex only through the ionized carboxyl group, but the degree of hypersensitive intensification achieved through this interaction is not noticeably altered when chelation is induced at higher pH. Similarly, no further change seems to be induced on changing the singly charged ligand chelate of the sugar acids in the "acid" complex to the doubly charged deprotonated ligand of the "neutral" complex. One must conclude that (a) the hypersensitive effect is produced primarily by substituting an anion for the neutral water molecule (giving, if nothing else, a strong-field distortion) and that (b) the quantitative hypersensitive influence varies with certain details of the structure of the anion (since carboxyl of an amino acid has different influence than carboxyl of a sugar acid).

Complexing the zwitterionic amino acid to Eu(III) through the carboxyl alone suffices to give a circular dichroism, which is strongest in the $^5D_1$ band. The "acid" complex of gluconic acid also has its strongest dichroism in this band (and it is almost true for the galactonic acid complex), even though for these sugar acids the evidence of the sign of the CD (inverted between gluconic and galactonic acids) says that chelation has taken place. This $^5D_1$ spectral transition is sharp, and its intensity seems unaltered by the complexing which produces hypersensitive intensification in other transitions. Futher, when the pH is raised, so that chelation occurs with the amino acid and deprotonation (presumably with strengthened bonding) of the sugar acid occurs, not only does the CD for this transition intensify appreciably, but for both types of ligand, the sign *inverts*. The absorption, however, remains without visible alteration. The CD is reasonably intense relative to the absorption ($\Delta\epsilon/\epsilon$ = *ca.* 0.02 for the neutral gluconate complex), whereas for the hypersensitive $^5D_0$ and $^5D_2$ it seems to be negligible. The $^5D_4$, which like the $^5D_1$ shows constant absorption (but some 10 times more intense), has its strongest CD with the alanine complex but the $\Delta\epsilon/\epsilon$ is still perhaps a factor of 10 smaller than for the $^5D_1$. Other transitions which seem to have relatively high $\Delta\epsilon/\epsilon$ values are the (($^5D_1$)) and ($^5D_2$) bands, which of course are structured, arising from $J = 2$ and $J = 1$ lower states, respectively, and the $^3D_3$ or (($^5L_6$)).

As with Pr(III), the CD patterns for the "neutral" complexes of gluconic and galactonic acids are sign-inverted, confirming chelation through the γ-hydroxyl group. Contrasting with the Pr(III) situation, the "acid" complexes also show a gluconic–galactonic CD sign difference, confirming the γ chelation that was only inferred in the Pr(III) case. The sign of the CD for the amino acid compexes (*e.g.*, alanine) matches that of the gluconic acid complex in the corresponding pH range, as was true for the $^3H_4 \rightarrow {}^3P_0$ of Pr(III) also.

Most significant would seem to be the differences in the CD details between closely related ligands. Not only do the gluconate and galactonate, differing only in configuration at the γ-carbon, have inversions of the signs of comparable CD transitions, but also at certain spectral transitions the CD of one may show splitting where the complex with the other ligand does not. Significant differences in relative intensities of CD components are also seen. It is therefore no surprise that there are differences of similar sorts between alanine and the hydroxy acids and between alanine and serine. The most prominent of the differences alluded to appear in the region 25,000–28,000 cm^{-1}, where transitions are dense, but they can also be found in the isolated transitions of the lower frequency portion of the spectrum.

A significant puzzle relates to the change in CD pattern of the amino acid complexes on chelation. This, for the change from purely carboxyl binding to chelation through the amino and carboxyl groups, is essentially identical with the CD change for the hydroxy acids from chelation to the singly ionized ligand to the doubly charged ligand following hydroxyl deprotonation. The final product in the amino acid case is the apparent analog of the starting configuration in the hydroxy acid system, which is the source of the puzzlement.

It may be that the obvious answer is the correct one, that the strength of chelation with an amino group involved is comparable to that of the doubly charged hydroxy acid ligand, rather than to that of the alcoholic

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(8) W. T. Carnall, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, **66**, 2159 (1962).

(9) W. T. Carnall, private communication.

hydroxyl. The formation of a five-membered ring in the amino acid chelate rather than the seven-membered chelate of the hydroxy acids may be a factor which reinforces this relation. The analogies between the two neutral-region CD spectra are too close, and the differences from the acid-region spectra too great, however, for acceptance of this explanation without at least considering some alternatives.

One alternative possibility, with hydrolyzable metal ion involved, is that hydroxyl binding to the metal ion, in the neutral region, is the differentiating factor. There is too big a gap, however, between the approximate pH of 5 at which the galactonate complex is converted to the strong-CD form and the pH of almost 7 for the alanine complex for this to be the answer. A variant of this might possibly merit more consideration —that the strong-CD forms require binding of two negative charges, in addition to chelation. With the sugar acids, the second negative charge comes with deprotonation of the ligand itself; for the amino acid, the relatively high pH needed to form the chelate would facilitate binding a hydroxyl group to the central ion to give the second charge. Perhaps still another way to consider the amino–hydroxyl difference is in terms of the effect in the acid complex of the protonic charge which is *to be* displaced on going from the acid-region to the neutral-region complex, equating the proton of the hydroxyl group to that on the $-NH_3^+$ group of the amino acid. The possibility of actual deprotonation of the amino group to an imine, to give the analog of the doubly charged sugar acid ligand, seems too remote on chemical grounds but could at least be susceptible to verification by infrared spectral or other techniques. Literature titration investigations of which the author is aware[10,11] are not sufficient to define closely the chemistry in the critical neutral region, and performance of such measurements may be advisable.

The tendency for CD transitions to be split into positive–negative pairs emphasized in prior papers is exhibited here also and still requires theoretical attention.

Acknowledgment.—Great appreciation must be expressed to Dr. W. T. Carnall for directing our attention to Eu(III) and for many helpful discussions.

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The Effect of High Pressure on Internal Vibrations of Nitrogen Heterocyclic Ligands and Their Metal Complexes[1a]

BY RICHARD BAYER[1b] AND J. R. FERRARO

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The effect of high pressure on the internal vibrations of pyrazine (1,4-diazine), of 2,2′-bipyridyl, and of some of the metal complexes of these ligands was investigated. Three types of behavior are noted under pressure: (1) all vibrations broaden and decrease in intensity; (2) some doubling of bands occurs; (3) blue shifts are observed. Certain pressure-sensitive vibrations are noted in the ligands and the complexes. The pressure effect on the ligand vibrations is greater than on the vibrations of the complexes.

Introduction

Several early studies of the effects of external pressure on the infrared spectra of various compounds have been made.[2–4] Other studies have since been reported.[5–8] Systematic studies on the effects of external pressure on molecular vibrations in the infrared region of 1600 cm^{-1} and lower have been neglected. This paper is a preliminary report of a study of the effects of pressure on internal vibrations of two organic ligands and several of their metal complexes in the region 400–1600 cm^{-1}.

Experimental Section

Reagents.—The pyrazine (1,4-diazine) was obtained from Aldrich Chemical Co., Milwaukee, Wis. It had a melting point of 52°, as obtained by a melting point block. The 2,2′-bipyridyl was obtained from Aldrich Chemical Co. and melted at 68°. The complexes used in this work were prepared and reported elsewhere.[9]

Infrared Measurements.—The infrared studies were conducted with an oversized Beckman IR-12 equipped with an 8X beam

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(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commision. Presented at the 157th National Meeting of the American Chemical Society Minneapolis, Minn., April 13–18, 1969. (b) At ANL on a Research Participation Program.

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