a quantitative interpretation is clearly not yet possible because of the present incomplete understanding of the complexity and relative importance of the several terms in the Ramsey equation. Interestingly, decreased ^{17}O nuclear shielding has been correlated[47-49] with increased Mo=O π-bond strength, an effect which was related to the angular momentum term in the Ramsey equation.[49]

Summary

The [(arene)Mo(CO)$_3$] derivatives give high-quality ^{95}Mo NMR spectra characterized by significant molybdenum shielding and well-separated narrow signals. Resolution of signals due to the various arenes and ready discrimination between isomers are thus possible. Considerable spectral simplification relative to ^1H and ^{13}C NMR is obvious, and there is no evidence for arene exchange below 38 °C. The foregoing illustrates the complementary information available with the use of ^{95}Mo, ^{13}C, ^{17}O, and ^1H NMR, and in fact with the present study, all nuclei of the (arene)Mo(CO)$_3$ molecules have been probed by NMR spectroscopy.

In the present [(arene)Mo(CO)$_3$] system, there are two effects which determine the observed ^{95}Mo chemical shift. First, and most importantly, the well-established charge donation from the arene to molybdenum results in these arene derivatives, *as a class*, having shielded molybdenum nuclei (with respect to those of other classes such as carbonyl phosphites,[2] carbonyl alkyls,[4] molybdates,[1] etc.). Second, more subtle bonding effects around molybdenum causes ordering of $\delta(^{95}Mo)$ *within* this class of compounds. In particular there is an interesting correlation between the ^{95}Mo nuclear shielding and Mo–arene bond strength.

It is important to note, however, that inversion in substituent chemical shifts and bond order/chemical shift relationships are known.[50-52] The ^{95}Mo chemical shifts of less than 50 compounds have so far been reported, and further development of the ^{95}Mo NMR chemical shift scale and an adequate theory of chemical shifts in quadrupolar nuclei must precede a more complete understanding of the ^{95}Mo chemical shift.

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Registry No. (cht)Mo(CO)$_3$, 12125-77-8; (mes)Mo(CO)$_3$, 12089-15-5; (*m*-xyl)Mo(CO)$_3$, 12288-65-2; (*p*-xyl)Mo(CO)$_3$, 12093-13-9; (*o*-xyl)Mo(CO)$_3$, 12288-64-1; (tol)Mo(CO)$_3$, 12083-34-0; K[(η^5-C$_5$H$_5$)Mo(CO)$_3$], 62866-01-7; Na[(η^5-C$_5$H$_5$)Mo(CO)$_3$], 12107-35-6; Mo(CO)$_6$, 13939-06-5.

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Dynamic ^1H Nuclear Magnetic Resonance Line-Broadening Study of Adduct Formation between Azidocobalt(III) Complexes Containing Organic Ligands and Lanthanide Shift Reagent

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The interaction of Eu(fod-d_9)$_3$ with a series of cobalt(III) complexes [of which (pyridine)azido[*N*,*N'*-ethylenebis(acetylacetoniminato)]cobalt(III) is the parent complex] in CDCl$_3$ has been investigated by using ^1H (and ^{13}C) NMR. The addition of Eu(fod-d_9)$_3$ results in induced shifts in the spectra of the respective cobalt complexes, and 1:1 adduct formation has been shown to occur in each case. Certain proton signals were found to broaden initially and then narrow as Eu(fod-d_9)$_3$ was incrementally added. Maximum broadening occurred when the Eu(fod-d_9)$_3$:cobalt complex ratio was between 0.3 and 0.4. From the concentration dependence of the chemical shifts, together with the observed line widths, the lifetimes of the adducts have been calculated; lifetimes of 10^{-3}–10^{-4} s were obtained. The study provides new examples of the nondilute case of fast-exchange line broadening—a case little studied in the past.

Introduction

Since their introduction in 1969,[1] lanthanide shift reagents (LSRs) have been routinely used to simplify the NMR spectra of organic compounds containing suitable heteroatoms.[2,3] To a lesser extent these reagents have also been employed in NMR studies of organometallic compounds,[3,4] but only isolated examples of their use for similar studies involving coordination complexes have appeared.[5-7] For example, LSRs have been employed to distinguish between N-bonded and S-bonded thiocyanato ligands[5] in suitable metal complexes as binding of the LSR only occurs to the uncoordinated nitrogen atom when the thiocyanate is S bonded. When the thiocyanate is N bonded, no interaction occurs. As in the above example, most of the studies with organometallic complexes have involved interaction of the LSR at heteroatom sites other than the donor atoms of the particular ligand present. Nevertheless, in previous papers[8-11] we have described studies in which co-

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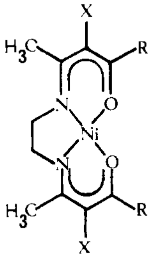
ordination via lone-pair-electron density on oxygen donor atoms of coordinated organic ligands does occur with the LSR Eu(fod)$_3$ such that lanthanide-induced shifts occur in the NMR spectrum of the bound organic ligand involved. Such adduct formation is qualitatively similar to the weak self-association via bridging oxygen atoms shown to occur under certain conditions in solution for LSRs such as Eu(fod)$_3$.[12] In our previous studies, the interaction of Eu(fod)$_3$ with complexes of type I[8,11] as well as with a series of tris(β-diketonato)cobalt(III) complexes[9,10] of type II in CDCl$_3$ has been investigated. In both cases 1:1 adduct formation was observed, and the evidence suggested that symmetrical adducts, involving donation from two oxygens for complexes of type I or three oxygens (about one octahedral face) for complexes of type II, occur. The 1:1 adduct of tris(pentane-2,4-dionato)cobalt(III) and Eu(fod)$_3$ has been isolated and has been shown by X-ray diffraction[9] to exhibit C_3 symmetry; the structure consists of an octahedron of oxygen donor atoms around the cobalt atom sharing a face with a tricapped trigonal prismatic arrangement of oxygens around the europium atom of the LSR. By choice of appropriate complexes, it has been possible to demonstrate the influence of both steric and electronic effects on the lanthanide-induced shifts; the technique has also proved useful for conformational studies of the coordinated ligands as well as for the investigation of metal complexes containing chiral centers (using optically active shift reagents).[8]



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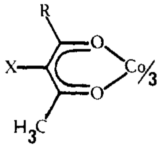


R= alkyl, aryl, CF$_3$
X= Cl, Br

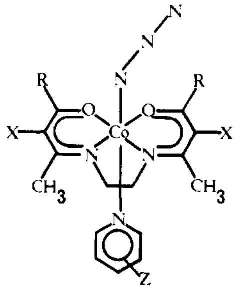
II

For a range of complexes of types I and II, kinetic aspects of the complex–LSR interaction have been studied.[8-11] For the β-diketone complexes, unusually slow chemical exchange at ambient temperature was observed[10] whereas selected complexes of type I yielded new examples of the nondilute case of fast-exchange line broadening.[11,13]

We now present the results of an investigation of the interaction of Eu(fod-d_9)$_3$ with a range of cobalt(II) complexes of type III. Such complexes are ideal for use in an extension of the above NMR studies since they are diamagnetic, kinetically inert, and soluble in nonpolar solvents such as CDCl$_3$ and appeared capable of presenting either two oxygens or two oxygens and a terminal azido nitrogen for bridge formation to an interacting Eu(fod-d_9)$_3$ molecule.[14] In addition, the wide variation of substituents on the organic ligands gives scope for a fuller study of the effects of structural influences on the nature of the complex–LSR interaction.

Experimental Section

Reagents and Techniques. Eu(fod-d_9)$_3$ and Eu(fod)$_3$ (Merck Sharpe and Dohme Ltd.) were dried over P$_2$O$_5$ in a vacuum at 120–130 °C for at least 24 h before use. Deuterated chloroform (Koch Light Laboratories) was stored over freshly dried anhydrous sodium bicarbonate and/or magnesium turnings to remove any phosgene or hydrogen chloride and was dried over Linde 3A molecular sieves before use. All transfers of the dried shift reagent were carried out in a glovebox containing dry nitrogen. All shift reagent runs were performed as described previously by using solutions that were 0.05–0.1 M in complex.[10] ^{1}H NMR spectra were obtained with a JEOL JNM-NH-100 continuous-wave spectrometer, and, as a check, several studies were also repeated (under similar conditions) with a JEOL JNM FX-60Q F/T spectrometer. Identical results were obtained with both instruments. All temperatures are ±1 °C and were measured either with a Wilmad probe thermometer or by using the usual ethylene glycol (near ambient temperature) or methanol (low temperature) calibration procedure; unless otherwise stated, runs were carried out at 33 °C. Chemical shifts are relative to tetramethylsilane as internal standard. Each line-broadening study was repeated between 2 and 12 times, and the quoted line widths are the means of all determinations; accurate line widths were obtained from expanded spectra. Lifetimes for each run were calculated by using at least four points between LSR:complex ratios of 0.1 and 0.7. Each quoted value is the mean (and standard deviation) of all points obtained from the multiple runs. Activation plots were constructed from data obtained over a temperature range of a least 40 C°, and the data were processed with the aid of a linear least-squares program.



III

compd	R	X	Z
a	CH$_3$	H	H
b	C$_2$H$_5$	H	H
c	CH$_3$	Cl	H
d	CH$_3$	Br	H
e	CF$_3$	H	H
f	(CH$_3$)$_4$C	H	H
g	C$_6$H$_5$	H	H
h	CH$_3$	H	4-CH$_3$
i	CH$_3$	H	3-CH$_3$
j	CH$_3$	H	3-C$_2$H$_5$
k	CH$_3$	H	3-Br

Preparation of Complexes of Type III. The synthesis of the parent complex IIIa is described here. All other complexes in the series were prepared by a similar procedure from the appropriate reagents.

To a stirred suspension of [*N*,*N*′-ethylenebis(acetylacetoniminato)]cobalt(II) hydrate[15] (3.0 g) in acetone (160 mL) was added sodium azide (1.4 g) in water (20 mL) followed by pyridine (1.5 mL). Hydrogen peroxide (3.0 mL) was then added dropwise during which the red suspension dissolved to yield a dark brown solution. The reaction mixture was stirred for a further 1 h and then left in an open beaker for 12 h. Dark brown crystals were obtained. The product was initially purified by chromatography using a column (15 cm × 2.5 cm) of acid-washed alumina followed by recrystallization from a chloroform/petroleum ether mixture. Dark brown crystals were obtained. They were dried in vacuo over P$_2$O$_5$; yield 3.0 g. Analytical data for this and the other complexes in the series are summarized in Table I. Selected spectral data for the complexes are listed in Table II.

Isolation of the Adduct of IIIa with Eu(fod)$_3$. Solid Eu(fod)$_3$ in slight excess was added to a solution of IIIa in benzene. An equal volume of toluene was added, and dark brown crystals of adduct formed as the solution evaporated. The product was recrystallized from a benzene/toluene mixture. Anal. Calcd for Co-

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Table I. Elemental Analyses

complex		% C	% H	% N	% Co
IIIa	calcd	50.7	5.8	20.9	15.2
	found	50.6	5.8	20.9	15.1
IIIb	calcd	53.0	6.3	19.5	13.7
	found	53.1	6.4	19.3	13.3
IIIc[a]	calcd	36.6	3.8	14.2	
	found	36.7	3.8	14.4	
IIId[a]	calcd	31.8	3.2	12.4	
	found	31.6	3.2	12.3	
IIIe	calcd	40.0	3.4	16.5	11.5
	found	39.8	3.4	16.2	11.5
IIIf	calcd	56.8	7.3	17.3	12.1
	found	56.7	7.3	17.0	12.0
IIIg	calcd	61.6	5.2	16.0	11.2
	found	61.4	5.2	15.8	11.2
IIIh	calcd	51.9	6.1	20.2	14.1
	found	52.0	6.1	20.0	14.1
IIIi	calcd	51.9	6.1	20.2	14.1
	found	51.9	6.2	20.3	14.0
IIIj	calcd	53.0	6.3	19.5	13.7
	found	52.8	6.7	19.6	13.6
IIIk	calcd	42.4	4.6	17.5	12.3
	found	42.2	4.8	17.3	12.4

[a] Analytical data are for the chloroform solvate.

Table II. Infrared and Visible Spectrophotometric Data for the Complexes

complex	ν_{N_3}, cm^{-1}	λ_{max},[a] nm	ϵ, M^{-1} cm^{-1}
IIIa	2024	452	1926
IIIb	2025	452	1821
IIIc	2023	463	1821
IIId	2024	460	1832
IIIe	2025	425	2572
IIIf	2027	450	1477
IIIg	2023	*b*	
IIIh	2025	452	2013
IIIi	2024	452	1928
IIIj	2025	452	1921
IIIk	2023	457	1906

[a] All bands overlap with the tail of an intense charge-transfer band in the ultraviolet region. [b] The λ_{max} of this peak is masked by a charge-transfer band.

$(C_{17}H_{23}N_6O_2)\cdot Eu(C_{10}H_{10}F_7O_2)_3$: C, 39.2; H, 3.7; Co, 4.1; N, 5.8. Found: C, 39.0; H, 3.7; Co, 4.3; N, 5.8.

Results and Discussion

Structure of the Cobalt Complexes. Solutions of the complexes in chloroform all yielded similar visible spectra (with a broad d–d band at ~450 nm) and exhibited azide stretches in the infrared near 2025 cm^{-1} (both in the solid and in solution), which are characteristic of coordinated azido ligands.[16] A summary of these results is given in Table II. It is evident from these data, taken together with the microanalytical results (Table I) and the NMR spectra (see later), that all complexes in the series have similar structures. An X-ray diffraction study[17] on the parent complex IIIa confirms that it has a trans-octahedral structure. The axial azido group is linear and shows unequal bond lengths between the nitrogens. The Co–N–N bond angle is 116.9° and points toward the oxygen donor side of the complex such that, on projection, it almost bisects the O–Co–O bond angle. The relative positions of the terminal nitrogen atom of the azido group and the two oxygen donors of the quadridentate ligand are such that simultaneous coordination by all three to the europium of Eu(fod)$_3$ appears possible.

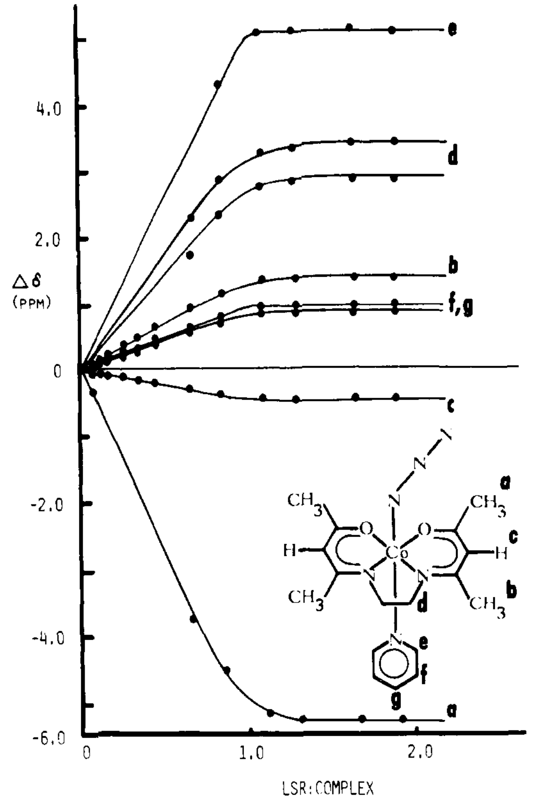

Figure 1. Chemical shifts induced by Eu(fod-d_9)$_3$ in the ^{1}H NMR spectrum of IIIa in CDCl$_3$.

The ^{1}H and ^{13}C NMR spectra of the complexes in CDCl$_3$ also confirm a trans-octahedral geometry in each case since, for example, each spectrum contained a single resonance for the –CH= groups; cis configurations would be expected to lead to two separate resonances for these groups. Similarly, for the complexes containing quadridentate ligands derived from pentane-2,4-dione, two methyl resonances were observed rather than the four that would be expected if one of the two possible cis configurations were adopted. A compilation of the NMR spectral data is given in Tables III and IV.

The ^{1}H spectrum of IIIa is representative of all the complexes. The singlet at 5.08 ppm corresponds to the =CH– protons; the four ethylenediamine backbone protons give multiplets at ~3.23 and ~3.78 ppm. The pyridine protons appear as two triplets and a doublet at 7.19, 7.67, and 7.95 ppm, respectively. Signals at 2.22 and 2.28 ppm are assigned to the two sets of CH$_3$ protons.[18] Because of their small chemical shift difference, it was not possible to assign these resonances unambiguously to individual methyl groups directly from the spectrum even though such assignment was desirable in view of the planned use of these complexes for the NMR line-broadening studies described subsequently. However, the use of Eu(fod-d_9)$_3$ has enabled assignment of these signals.

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(18) Relative to those of IIIa, the chemical shifts of the two methyl signals move downfield on replacement of the methine protons by chloro (IIIc) or bromo (IIId) groups. Similarly, substitution of CF$_3$ groups (IIIe) for the methyl groups adjacent to the oxygen donors also results in a significant downfield shift of the signal for the methine protons as well as for the signal for the methyl groups adjacent to the nitrogens. These observed downfield shifts no doubt reflect deshielding resulting from the presence of electron-withdrawing groups. Replacement of coordinated pyridine by one of a range of substituted pyridines causes only very small changes in the chemical shifts of the methyl and methine protons of the quadridentate ligands. This result parallels that observed previously for related complexes of type CoX$_3$(substituted pyridine)(β-diketonato)$_2$ where X = N$_3^-$, NO$_2^-$, CN$^-$ (see: Boucher, L. J.; Paez, N. G. *Inorg. Chem.* **1971**, 1680–1685. Boucher, L. J.; Herrington, D. R. *Ibid.* **1972**, *11*, 1772–1777. Boucher, L. J.; Battis, E. J.; Paez, N. G. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1373–1387).

Table III. ^{1}H NMR Assignments for the Complexes[a,b]

complex	$CH_3(O)$	$CH_3(N)$	=CH-	$-(CH_2)_2-$	aromatic protons	CH_3-py
IIIa	2.22 (s)	2.28 (s)	5.08 (s)	3.23 (m), 3.78 (m)	7.19 (t), 7.67 (t), 7.95 (d)	
IIIb	1.19 (t), 2.51 (q)[c]	2.27 (s)	5.04 (s)	3.19 (m), 3.82 (m)	7.17 (t), 7.66 (t), 7.98 (d)	
IIIc	2.49 (s)	2.59 (s)		3.39 (m), 3.95 (m)	7.27 (t), 7.74 (t), 7.87 (d)	
IIId	2.59 (s)	2.66 (s)		3.42 (m), 3.95 (m)	7.28 (t), 7.75 (t), 7.89 (d)	
IIIe	*d*	2.38 (s)	5.43 (s)	*d*	*d*	*d*
IIIf	1.25 (s)[e]	2.26 (s)	5.06 (s)	3.44 (m), 3.83 (m)	7.15 (t), 7.65 (t), 8.00 (d)	
IIIg		2.44 (s)	5.77 (s)	3.35 (m), 3.88 (m)	7.14-8.13 (m)	
IIIh	2.23 (s)	2.28 (s)	5.06 (s)	3.24 (m), 3.78 (m)	7.01 (d), 7.78 (d)	2.33 (s)[f]
IIIi	2.23 (s)	2.28 (s)	5.06 (s)	3.22 (m), 3.78 (m)	7.06 (t), 7.45 (d), 7.72 (d), 7.75 (s)	2.23 (s)
IIIj	2.22 (s)	2.27 (s)	5.05 (s)	3.21 (m), 3.76 (m)	7.07 (t), 7.47 (d), 7.71 (d), 7.78 (s)	1.14 (q), 2.54 (t)[f]
IIIk	2.24 (s)	2.31 (s)	5.01 (s)	3.26 (m), 3.81 (m)	7.10 (t), 7.83 (d), 7.93 (d), 8.08 (s)	

[a] In ppm relative to tetramethylsilane. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; all resonances showed relative intensities in accord with the above assignments. [c] CH_3CH_2. [d] Because of the very low solubility of this complex, assignment proved difficult. [e] $(CH_3)_3$. [f] CH_3CH_3.

Table IV. ^{13}C NMR Assignments for the Complexes[a-c]

complex	(O)*C*R	(N)*C*CH_3	(O)C*C*H_3	(N)C*C*H_3	=CH-	$(CH_2)_2$	aromatic carbons	CH_3-py
IIIa	167.6	180.2	26.2	22.5	95.3	52.7	124.3, 137.6, 152.3	
IIIb	167.6	180.6	12.4, 32.8[d]	22.6	93.7	52.6	124.1, 137.6, 152.3	
IIIc	167.6	177.4	27.5	21.3		53.9	124.8, 138.2, 151.7	
IIId	(?)	178.5	29.3	24.3		54.6	124.9, 138.3, 151.7	
IIIf	167.3	189.7	29.0, 39.5[e]	22.6	90.1	52.8	124.3, 138.5, 152.2	
IIIg	168.4	174.9		22.9	93.8	52.9	124.3, 137.5, 152.1	
IIIh	167.5	180.0	26.1	22.4	95.2	52.6	125.2, 149.6, 151.6	20.8
IIIi	167.6	180.1	26.1	22.4	95.2	52.7	123.7, 134.3, 138.3, 149.5, 152.5	18.8
IIIj	167.5	180.0	26.1	22.4	95.2	52.7	123.8, 137.1, 140.1, 149.6, 151.8	14.5, 26.0[f]
IIIk	167.9	180.3	26.2	22.5	95.4	52.7	120.1, 124.9, 140.4, 150.4, 153.4	

[a] In ppm relative to tetramethylsilane. [b] In all cases the splitting patterns observed in the corresponding off-resonance spectra were in accord with the proposed structures. [c] Complex IIIe was of too low solubility to obtain the ^{13}C NMR spectrum. [d] CH_3CH_2. [e] $(CH_3)_3C$. [f] CH_3CH_2.

Incremental addition of Eu(fod-d_9)$_3$ to a solution of IIIa in $CDCl_3$ (Figure 1) resulted in the higher field methyl resonance moving further upfield (with considerable broadening) while the other methyl signal moved downfield (with less broadening).[19] A parallel experiment using IIIb was carried out, and the ethyl signals (a triplet and a quartet) moved upfield while the methyl signal (a singlet) moved downfield. Thus, by comparison, the low-field methyl resonance of IIIa (which is shifted downfield) almost certainly corresponds to the methyl groups adjacent to the nitrogen donors. The methyl signals of the other complexes of type III were assigned similarly (Table III).

Assignments of certain resonances in the ^{13}C NMR spectra have also proved possible with the aid of LSR.[20] Addition of Eu(fod)$_3$ to a solution of IIIa caused shifts of all resonances in the ^{13}C NMR spectrum (Figure 2). The limiting induced shift (corresponding to complete adduct formation) of the carbon resonance originally at 167.6 ppm was 2.6 ppm further downfield than that for the carbon resonance at 180.2 ppm. Its greater limiting shift suggests that this carbon signal at 167.6 ppm arises from the (equivalent) carbons adjacent to the oxygens (since these carbons are closer to the site of attachment of the LSR).

Similarly, the shift to higher field of the methyl resonance at 26.2 ppm on addition of LSR is in accord with this signal arising from the methyl groups closest to the site of attachment of the LSR provided a significant contact mechanism operates in this system (see later).

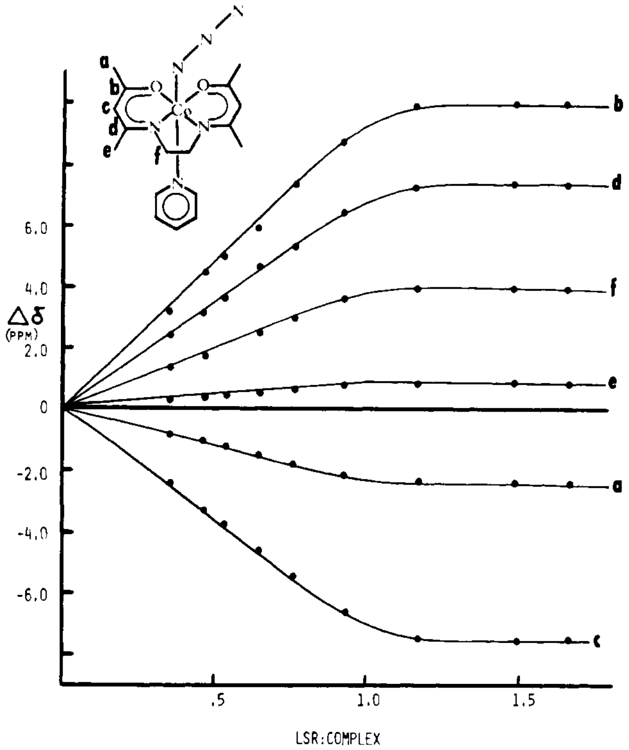

Figure 2. Chemical shifts induced by Eu(fod)$_3$ in the ^{13}C NMR spectrum of IIIa in $CDCl_3$.

The Nature of the Cobalt Complex–LSR Interaction. Addition of Eu(fod-d_9)$_3$ to the parent complex (IIIa) in $CDCl_3$ results in a linear dependence of the ^{1}H induced shift on Eu(fod-d_9)$_3$ concentration up to a LSR:complex ratio approaching 1, with the limiting shifts occurring shortly after the 1:1 ratio is attained (Figure 1). Such behavior provides strong evidence that the adduct formed between IIIa and Eu(fod-d_9)$_3$ is of 1:1 stoichiometry. The results from a parallel study in which the induced shifts in the ^{13}C NMR resonances

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(19) So that it could be ensured that no crossover of methyl signals occurred, very small increments of Eu(fod-d_9)$_3$ were added initially.

(20) However, the interpretation is somewhat more complicated in this case by the presence of new carbon signals, which originate from the LSR.

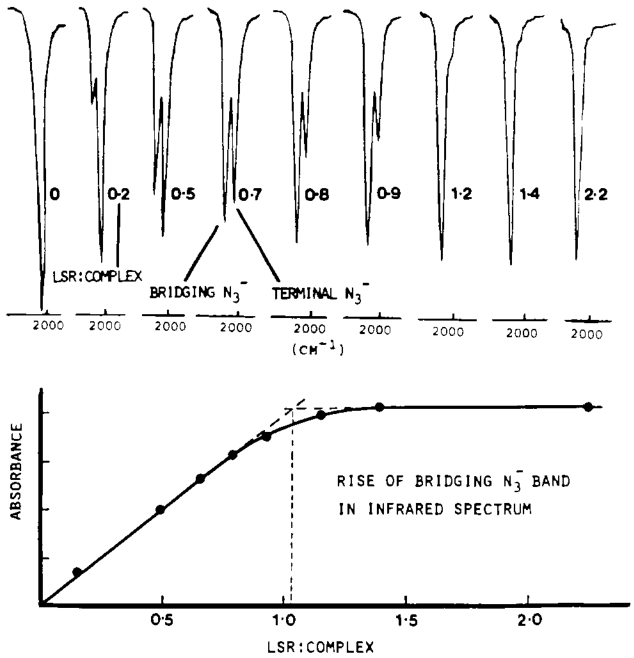


Figure 3. Effect of addition of Eu(fod)$_3$ on the azido stretching frequency in the infrared spectrum of IIIa in CDCl$_3$.

were followed (Figure 2) lead to a similar conclusion.

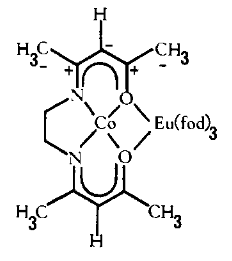
The induced ^{1}H and ^{13}C chemical shift patterns for the coordinated *N,N'*-ethylenebis(acetylacetoniminato) ligand in IIIa (Figures 1 and 2) are somewhat different from those obtained previously on interaction of Eu(fod)$_3$ with the square-planar nickel complex of type I, for which, on adduct formation, the europium ion was postulated to be bound to the two oxygens of the quadridentate ligand.[8] Since the relative magnitudes of the lanthanide-induced shifts are expected to be sensitive to the geometry of the LSR–substrate adduct,[2,21] the above observation is in accord with altered relative positions for the europium ion and the coordinated quadridentate ligand in the adduct of IIIa (relative to the adduct of I).

Infrared spectroscopy has proved a useful technique for probing the possible involvement of the azido group of IIIa in adduct formation. Coordinated azido groups normally display an asymmetric stretching frequency in the approximate range 2100–2010 cm^{-1}; the frequency tends to be higher for bridged azido groups than for terminally coordinated ones.[16,22]

The changes in the infrared spectrum in the azide stretching region when Eu(fod)$_3$ is added incrementally to IIIa in CDCl$_3$ are shown in Figure 3. On successive addition of Eu(fod)$_3$ the initial azido peak at 2024 cm^{-1} decreases in intensity while there is a concomitant rise of a new peak at 2058 cm^{-1}) which is assigned to the bridging azido group. When greater than a 1:1 molar ratio of LSR to cobalt complex is reached, only the new signal remains. Clearly these changes are consistent with participation of the azido group in bridge formation to the LSR. In addition, the 1:1 stoichiometry of the interaction is confirmed by the absence of further change (slightly) after 1:1 ratio of LSR to complex is attained.

As for the adduct of II with Eu(fod)$_3$,[8] the corresponding adduct of IIIa was also successfully crystallized and was found to have the expected 1:1 stoichiometry. In confirmation of the trends observed in the solution infrared studies, the azido asymmetric stretching modes for the solid compounds (Nujol mulls) occur at 2022 cm^{-1} for IIIa but at 2060 cm^{-1} for its adduct with Eu(fod)$_3$. The ^{1}H NMR spectrum of the solid adduct dissolved in CDCl$_3$ is identical with the spectrum obtained for a freshly prepared mixture of the complex and Eu(fod)$_3$ in this solvent, thus confirming that the integrity of the adduct is maintained during the isolation procedure.

As in our studies[8,10] involving complexes of types I and II, a preliminary attempt to fit the observed NMR induced shifts for IIIa to a pseudocontact (through-space) model based on the McConnell–Robertson equation[21] was unsuccessful, and the presence of a contact contribution to the induced shifts seems likely. ^{13}C NMR spectroscopy provides a convenient method for investigating the presence of a contact (through-bond) term in the induced shifts; the chemical shifts of the carbon backbone of a substrate coordinated to a paramagnetic LSR have been shown to be especially sensitive to the effects of such a mechanism.[8,23] This is particularly so if conjugation, as occurs in the β-diketone-derived sections of the quadridentate ligand of IIIa, is present. The absolute magnitude of such a contribution usually diminishes along a carbon chain as the number of covalent bonds linking successive carbons to the LSR increases; however, the sign of the contact term is expected to alternate along such a chain.[3] Thus a possible result of any contact contribution on the ^{13}C NMR spectrum of IIIa is illustrated by IV; a minus sign indicates an induced shift to higher field (that is, in a direction which opposes the usual direction of pseudocontact shift using europium LSRs). Of the carbon atoms whose resonances are likely to exhibit contact shifts to higher fields, only that of the –CH= group forms part of the ligand's conjugated system and hence might be expected to be especially affected by any contact term present. In accord with this, the resonance resulting from this carbon does show a large upfield shift (terminal value of −7.5 ppm) whereas the resonance corresponding to the methyl groups adjacent to each oxygen donor site is also shifted to higher fields but to a lesser extent (Figure 2). These observations are thus consistent with the presence of both pseudocontact and contact interactions although it is not possible with the available data to partition a particular observed induced shift into components that correspond to each of these mechanisms.



IV

Using the NMR and IR data for IIIa in CDCl$_3$ discussed above, attempts to calculate an equilibrium constant for the formation of the 1:1 adduct were unsuccessful. It is evident that the *K* value is high ($>10^3$ M^{-1}), and hence the adduct is close to completely formed throughout the LSR addition.[24]

Exchange Line-Broadening Studies Involving IIIa. The line width of each ^{1}H NMR signal for IIIa in CDCl$_3$ was found

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(21) McConnell, H. M.; Robertson, R. E. *J. Chem. Phys.* **1958**, *29*, 1361–1365.

(22) It is pertinent to the present study that LSR has been shown previously to interact with a metal-bound azido group: Marks, T. J.; Kristoff, J. S.; Alich, A.; Shriver, D. F. *J. Organomet. Chem.* **1971**, *33*, C35–C37.

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(24) A similar situation was found to occur even when a 10^{-3} M concentration of complex was used in a related (FT) NMR experiment, and hence no accurate measurement of the *K* value proved possible.

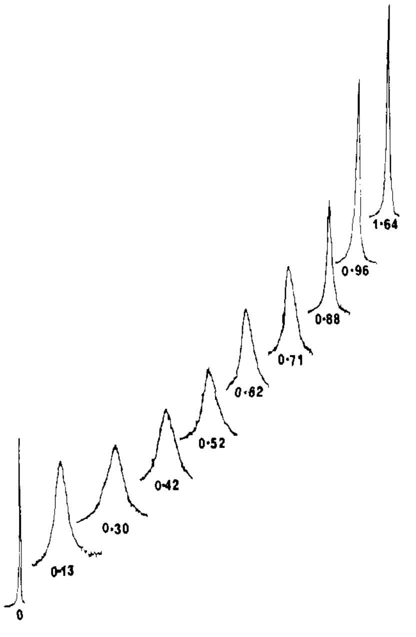

Figure 4. Effect of Eu(fod-d_9)$_3$ on the line widths of the ^{1}H NMR signal for the methyl groups adjacent to the nitrogen donors of the quadridentate ligand in IIIa (CDCl$_3$; 33 °C). The numbers under each curve are the [Eu(fod-d_9)$_3$]:[IIIa] ratios used.

to initially broaden and then narrow as Eu(fod-d_9)$_3$ was added incrementally; maximum line width occurred in each case when the Eu(fod-d_9)$_3$:complex ratio lay between 0.3 and 0.4. The extent of broadening of individual resonances for a given complex:LSR ratio varied considerably from one resonance to the next. The line width behavior of the methyl resonance arising from CH$_3^b$ (the methyl groups adjacent to the nitrogen of the quadridentate ligand) was chosen for detailed study. The effects of added LSR are illustrated in Figure 4. The line width narrows to a sharp peak soon after a molar ratio of 1 is reached, and no further change then occurs as further LSR is added.[25] At this stage adduct formation is complete, and it is significant that the half-width at half-height is now 1.3 Hz, which is only 0.4 Hz wider than that of this signal in the absence of adduct formation.[26]

The dynamic NMR behavior of IIIa on interaction with Eu(fod-d_9)$_3$ provides a new example of the unusual nondilute case of fast-exchange line broadening.[11,13] From the concentration dependence of the chemical shift and the line width, the lifetime of the adduct (and the rate constant for its dissociation) can be determined by using

$$\Delta\nu_{1/2} = f_A(\Delta\nu_A) + f_B(\Delta\nu_B) + f_A^2 f_B \tau_B (2\pi)\delta^2 \qquad (1)$$

where $\Delta\nu_{1/2}$ is the half-width of the observed resonance (in Hz) at half-height, $\Delta\nu_A$ is the half-width of the corresponding cobalt complex resonance in the absence of adduct formation, $\Delta\nu_B$ is the half-width on complete adduct formation, f_A is the mole fraction of free cobalt complex, f_B is the mole fraction of the cobalt complex as the LSR adduct, τ_B is the lifetime of the adduct, and δ is the difference between the original shift and the limiting chemical shift on complete adduct formation.

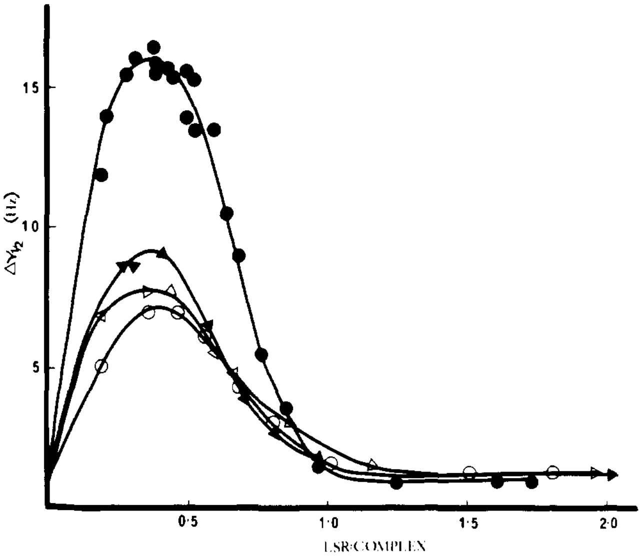

Figure 5. Effects of Eu(fod-d_9)$_3$ on the line widths (half-width at half-height) of the ^{1}H NMR signals of selected complexes of type III. The data correspond to the methyl protons adjacent to the nitrogens of the quadridentate ligand. ●, IIIa; △, IIIb; ▲ IIIc, ○ IIId.

$\Delta\nu_A$ was obtained directly from the observed line width when $\rho \simeq 2$ (ρ = [LSR]$_{total}$/[complex]$_{total}$), where adduct formation is essentially complete. The limiting chemical shift δ was obtained from graphical extrapolation of the chemical shifts of the methyl (CH$_3^b$) protons from below $\rho = 0.5$ to $\rho = 1.0$. For IIIa, a limiting shift of 144 Hz was obtained. By use of this value and the observed chemical shift for a particular value of ρ, the mole fraction f_B of the cobalt complex as the adduct can be calculated.[27] The analysis assumes that the adduct dissociation is a first-order process (as has been shown to occur for other LSR systems involving Eu(fod)$_3$]:[10,11,13]

$$\text{(Co complex)} + \text{LSR} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{(Co complex)–LSR}$$

From eq 1, a lifetime of 8.4×10^{-4} s was obtained for the adduct of the parent complex, IIIa. This corresponds to a first-order dissociation rate constant ($k_d = 1/\tau_B$) of 1.19×10^3 s^{-1}. Differentiation of the above line-broadening expression leads to the prediction that, provided the K value for 1:1 adduct formation is very large, maximum line width should occur when the LSR:complex ratio is 0.33.[11] The behavior of IIIa (Figures 4 and 5) is in accord with this prediction.

It appears significant that this system, which involves simultaneous coordination of two oxygens and one nitrogen to the LSR, gives longer lifetimes than the two oxygen donor systems[11] of type I (~10^{-5} s) but shorter lifetimes than those found for the three oxygen donor system[10] of type II (~10^{-2} s). Indeed, in all these case, the lifetimes are longer than reported for simple organic substrates containing only one site of attachment to the LSR.[13]

Effect of Ligand Substituents. In our previous studies[8,10] involving complexes of types I and II, it has been demonstrated that ligand substitution such as replacement of the methyl groups adjacent to the oxygen donors by bulky *tert*-butyl or electron-withdrawing CF$_3$ groups drastically reduces (or completely inhibits) interaction with LSR.

A related investigation of the effects of ligand substitution within the present series of complexes has also been undertaken. A comparative study of the interaction IIIb–IIId in

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(25) The CH$_3^a$ signal (methyl groups adjacent to the oxygen donor atoms) also behaves in a similar manner except that line broadening is much larger and the induced shift is upfield toward Me$_4$Si. The line width of this signal between the molar ratios of 0.2 and 0.6 was so extensively broadened under the conditions of the experiment that no accurate line width measurement was possible.

(26) This difference in line width can possibly be attributed to the presence of a barely significant contact contribution at this site, which is remote from the points of attachment to the LSR. The CH$_3^a$ methyl protons, which are closer to the sites of attachment to the LSR, exhibit a slightly broader resonance of ~2.0 Hz (half-width at half-height) on adduct formation.

(27) As in the previous study,[11] the δ value obtained by extrapolation yielded individual values for the lifetimes of the adduct that showed no systematic trends as ρ was varied.

Table V. Mean Lifetimes (τ_B)[a] of Adducts and Observed Limiting Induced Shifts for the Methyl Signals at 33 °C

complex	$10^4\tau_B$, s	$10^{-3}k_d$, s^{-1} [b,c]	$\delta\Delta$-($CH_3{}^b$)	$\delta\Delta$-($CH_3{}^a$)[d]
IIIa	8.4 ± 0.4[e]	1.19	1.37	−5.30
IIIb	3.6 ± 0.1	2.78	1.28	*f*
IIIc	3.4 ± 0.2	2.94	1.57	−6.62
IIId	3.1 ± 0.4	3.23	1.61	−6.82
IIIh	6.4 ± 0.3	1.56	1.38	−5.26
IIIi	3.5 ± 0.2	2.86	1.33	−4.98
IIIj	3.4 ± 0.6	2.94	1.34	−5.01
IIIk	5.8 ± 0.1	1.72	1.45	−5.70

[a] Data calculated from the line width behavior of the signal from the $CH_3{}^b$ groups adjacent to the nitrogens of the ethylenediamine backbone of the quadridentate ligand. [b] $k_d = \tau_B{}^{-1}$ = first-order reaction rate constant. [c] For IIIe–IIIg there was only weak interaction with LSR and limiting shifts were not reached—see text. [d] In ppm; a negative sign indicates a shift to high field. [e] As mentioned in the text, the line widths corresponding to the $CH_3{}^a$ protons were generally too broad to measure accurately. However, it was possible to obtain approximate half-width values for this proton signal when the LSR:complex ratios were 0.7 and 0.85. From these a mean value for τ_B of (8.1 ± 1.9) × 10^{-4} s was obtained. [f] Not applicable as this is the ethyl-substituted compound.

$CDCl_3$ with LSR indicates that the behavior of all these complexes is qualitatively similar to that just discussed for IIIa with fast exchange being observed in each case. Figure 5 illustrates the effects of added LSR on the half-widths (at half-height) of the respective $CH_3{}^b$ protons. As for IIIa, the final half-widths on complete adduct formation were in each case ca. 1.5 Hz; *K*, values for the complexes IIIa–IIId were all found to be > 10^3 M^{-1}. The calculated lifetimes are tabulated in Table V. Although caution needs to be exercised in ascribing the different observed lifetimes solely to either steric or electronic influences, it does seem likely that the reduction in lifetime for the adduct of IIIb over that of IIIa may reflect steric crowding by the ethyl groups at the sites of binding to the LSR. Similarly, for IIIc and IIId, the presence of electron-withdrawing substituents in the conjugated backbone of the quadridentate ligand appears to have electronic consequences, which result in the observed shortened lifetimes for the respective adducts.

The reaction of the $Eu(fod)_3$ with IIIe, which contains electron-withdrawing CF_3 groups adjacent to the donor oxygens, differs somewhat from the behavior discussed above. The low solubility of this complex in $CDCl_3$ precluded accurate line-broadening studies. Nevertheless, by use of the FT NMR technique, the proton spectrum of a dilute solution of the complex could be followed as $Eu(fod\text{-}d_9)_3$ was incrementally added. Only very small shifts were observed on each addition, and the shifts continued after the LSR:complex ratio had reached 6; it was not possible to obtain the limiting shift in this case. This behavior, together with the absence of a linear dependence of the lanthanide-induced shift on LSR concentration (even at low concentrations of the latter), indicates that the *K* value for adduct formation is small. For the square-planar nickel complex of this fluorinated ligand, no lanthanide-induced shifts were detected under conditions similar to those used in the present experiment.[8] For both systems the observed behavior can be attributed to the electron-withdrawing effect of the electronegative CF_3 groups, which will effectively reduce the electron density of the oxygen donors and hence influence their ability to coordinate to the LSR.[28]

Table VI. Temperature Variation of the First-Order Dissociation Rate Constant (k_d)[a] and Activation Parameters for Selected Adducts with $Eu(fod\text{-}d_9)_3$

adduct of IIIa		adduct of IIIc		adduct of IIIk	
T, K	$10^{-2}k_d$	*T*, K	$10^{-3}k_d$	*T*, K	$10^{-2}k_d$
289	5.99	289	1.74	289	9.1
296	8.16	296	2.11	296	12.8
306	11.9	306	2.94	306	17.2
311	14.8	316	3.90	316	22.0
316	16.1	329	5.83	329	32.7
329	23.5				
$\Delta H^{*b} = 25 \pm 4^d$		$\Delta H^* = 21 \pm 3$		$\Delta H^* = 22 \pm 3$	
$\Delta S^{*c} = -105 \pm 15$		$\Delta S^* = -111 \pm 15$		$\Delta S^* = -113 \pm 15$	

[a] In s^{-1}; calculated from the line width behavior of the signal from the $CH_3{}^b$ groups. [b] In kJ mol^{-1}. [c] In J K^{-1} mol^{-1}. [d] Assessed error.

As might be predicted from the previous studies,[8,10] bulky *tert*-butyl and aryl groups adjacent to the oxygen sites in IIIf and IIIg result in only very weak interaction of these complexes with LSR. Because of this, as well as observed additional complication in the line width behavior (perhaps associated with adduct formation affecting another dynamic process in these sterically hindered complexes), no estimate of the lifetimes of the adducts was attempted.

For investigation of the possible effects of substitution of the pyridine moiety of IIIa on the lifetimes of respective adducts, the complexes IIIh–IIIk were prepared. Substitution results in only small perturbations to the chemical shifts of the ^1H and ^{13}C NMR resonances of the coordinated quadridentate ligand (Tables III and IV), and the infrared asymmetric stretching mode of the azido group for the respective complexes exhibits little change along the series **IIIh–IIIk** (Table II). In parallel to this, the behavior of the individual complexes in this series toward $Eu(fod\text{-}d_9)_3$ is very similar. In all cases 1:1 adduct formation was observed with the adducts exhibiting *K* values of 10^3 M^{-1} or greater. The line width behavior for the respective complexes was similar to that discussed above for IIIa–IIId; the corresponding lifetimes for the adducts are given in Table V (and activation parameters for selected adducts in Table VI[29]). In each case the lifetime was found to be somewhat less than that of the parent compound although the difference in lifetimes between the complexes containing substituted pyridines is relatively small; there is no clear dependence on the respective donor abilities of the pyridines involved.

Concluding Remarks

The results discussed in this paper further extend our previous studies[8-11] to include the investigation of novel heterobridged LSR adducts. An electron-withdrawing substituent or a bulky group adjacent to the (oxygen) sites of attachment of the cobalt complex to the LSR reduces the stability of the corresponding adduct whereas substituents on other sites have much less effect. the study provides new examples of the unusual nondilute case of two-site fast-exchange line broadening since the appreciable concentrations of the free complex and its LSR adduct both contribute to the last term in eq 1. This, together with the longer lifetimes of the adducts (three sites of binding) and the generally large induced chemical shifts which are a feature of these LSR–complex systems (line broadening depends on the square of the induced shift on complete adduct formation), results in the last term in eq 1 having a significant influence on the line-broadening behavior.

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(28) Nevertheless, the absence of an interaction for the nickel complex with $Eu(fod)_3$ contrasts with the definite (although weak) interaction observed with IIIe. This different behavior most likely reflects the binding of the azido group in the latter complex, which, regardless of the participation of the oxygen atoms of the quadridentate ligand, is free to interact directly with the LSR.

(29) Comparison of the activation parameters for adduct dissociation of IIIa, IIIc, and IIIk (Table VI) indicates generally similar values, with the complexes incorporating electron-withdrawing groups showing lower ΔH^* values (but slightly less favorable ΔS^* values).

This term is negligible in the more commonly observed dilute case such as described by Swift and Connick[30] in which the paramagnetic shift reagent is present in much lower concentration than the diamagnetic substrate.

Registry No. IIIa, 64612-05-1; IIIb, 78685-54-8; IIIc, 78685-55-9; IIId, 78685-56-0; IIIe, 78685-57-1; IIIf, 78685-58-2; IIIg, 78685-59-3; IIIh, 78685-60-6; IIIi, 78685-61-7; IIIj, 78685-62-8; IIIk, 78685-63-9; Eu(fod)$_3$, 17631-68-4; [4,4'-(ethylenedinitrilo)di-2-pentanonato-(2−)]cobalt, 36802-26-3; [3,3'-(ethylenedinitrilo)di-3-hexanonato-(2−)]cobalt, 78685-64-0; [2,2'-(ethylenedinitrilo)di-3-chloro-2-pentanonato(2−)]cobalt, 78685-65-1; [2,2'-(ethylenedinitrilo)di-3-bromo-2-pentanonato(2−)]cobalt, 78685-66-2; [4,4'-(ethylenedinitrilo)di-1,1,1-trifluoro-2-pentanonato(2−)]cobalt, 35816-74-1; [5,5'-(ethylenedinitrilo)di-2,2-dimethyl-3-hexanonato(2−)]cobalt, 78685-67-3; [3,3'-(ethylenedinitrilo)di-1-phenyl-1-butanonato(2−)]-cobalt, 36802-28-5.

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Spectroscopic and Magnetic Properties of $Cs_3Ti_2Cl_9$

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The title compound has been obtained as large single crystals of good optical quality. A series of experiments have been performed on it, in a wide temperature range, in order to describe properly the ground state manifold on the $Ti_2Cl_9^{3-}$ binuclear unit. These include EPR, Raman, and infrared and visible absorption spectroscopy and magnetic circular dichroism (MCD) as well as magnetic susceptibility measurements. Among our results, infrared and magnetic data have been especially fruitful since they prove unambiguously that, for each of the $TiCl_6^{3-}$ units, the trigonal field is very large, with $^2A_1$ lying about 1500 cm^{-1} below ^2E. All our other data are consistent with that interpretation. The lowest lying terms in our system are therefore $^1A_1'$ and $^3A_2''$ arising from the exchange interaction between two $^2A_1$ states. An analysis of the temperature dependence of $\chi_\parallel$ and $\chi_\perp$ indicates very clearly that $^1A_1'$ is lowest, the energy gap $^1A_1'$–$^3A_2''$ being roughly $J = -525$ cm^{-1}. The above values for the trigonal field Δ and for J have been obtained on the basis of a static model, which we believe is essentially correct. In view however of a slight discrepancy between our susceptibility data and the model predictions, we searched for an improvement of the theory. We show that vibronic coupling might be responsible for the observed increase of $|J|$ when T is lowered from room to liquid helium temperature. Finally, the difference in behavior between $Cs_3Ti_2Cl_9$ and $Cs_3Cr_2Cl_9$ regarding the order of magnitude of exchange interactions is briefly discussed. Our EPR results indicate that $Cs_3Ti_2Cl_9$ is a very favorable matrix to study the coupling of any paramagnetic ions added intentionally.

Introduction

A great effort is presently being made toward a better understanding of the spectroscopic and magnetic properties of clusters of transition-metal ions. These serve as molecular models for checking physical concepts and are of some relevance to spin glasses. Among those clusters, the confacial, bioctahedral anions $M_2Cl_9^{3-}$ have long been known but they are still of current interest. Recent work includes, for example, the synthesis of ions containing two different metal atoms,[2] a reinvestigation of the crystal structure of $Cs_3Sc_2Cl_9$,[3] and answers to questions related to the optical spectra of molybdenum and tungsten derivatives.[4]

Among the $A_3M_2X_9$ (X = Cl, Br) structures, those with M = Cr,[5] Ti, or V (space group D_{6h}^4-$P6_3/mmc$ with $Z = 2$) deserve particular attention since they contain discrete, isolated dinuclear units of high symmetry (D_{3h}) having their threefold axis coinciding with the *c* axis of the crystal. By contrast with heavily doped matrices (e.g., Al_2O_3), which contain clusters of various symmetries, such materials are therefore ideally suited to a detailed investigation of exchange interaction within isolated pairs. Indeed, during the past few years, availability of single crystals of sufficient size has quite naturally stimulated a great deal of activity in this area.

The chromium derivatives have been chosen first since they present favorable circumstances from both an experimental and a theoretical viewpoint; Cr^{3+} is well-known to show sharp lines in its optical spectrum, and it has a spin-only ground state. Published work on the $Cr_2X_9^{3-}$ anions includes an analysis of their optical and magnetooptical properties in the visible and near-UV[6,7] and magnetic[8] and EPR[9] as well as Raman[10,11] and infrared studies.[10] All these measurements lead to an unambiguous description of the ground-state manifold and to detailed information regarding several excited spectroscopic terms of the chromium pairs.

From a theoretical viewpoint, the study of titanium pairs is challenging for especially two reasons. First, difficulties arise when both orbital and spin angular momentums have to be taken into account in the treatment of exchange interactions. Models have been proposed,[12-16] but they remained largely unexploited due to the paucity of experimental data. Previous work on $Cs_3Ti_2Cl_9$ or related systems has not been performed under ideal experimental conditions. Optical spectra have been taken on solids[17,18] or solutions,[2] but their dependence upon

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(1) (a) EPCI. (b) Université de Paris Sud.

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