(8) D. A. Deranleau, *J. Am. Chem. Soc.*, **91**, 4044–4050 (1969).
(9) (a) J. E. Fletcher, A. A. Spector, and J. D. Ashbrook, *Biochemistry*, **9**, 4580 (1970); (b) J. E. Fletcher and A. A. Spector, *Comput. Biomed. Res.*, **2**, 164 (1968); (c) M. E. Magar, R. F. Steiner, and J. E. Fletcher, *J. Theor. Biol.*, **32**, 59 (1971); (d) J. E. Fletcher, J. D. Ashbrook, and A. A. Spector, *Ann. N.Y. Acad. Sci.*, **226**, 69 (1973).
(10) It also argues against the possibility that the spectra are actually envelopes of closely spaced narrow lines. The observation that the entire broad envelope relaxed together in an inversion recovery experiment and the short time constant obtained from this experiment give additional evidence that the broad peak is indeed a single resonance.
(11) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
(12) (a) A. Allerhand, R. F. Childers, and E. Oldfield, *Ann. N.Y. Acad. Sci.*, **222**, 764 (1973); (b) R. S. Norton and A. Allerhand, *J. Am. Chem. Soc.*, **98**, 1007 (1976).
(13) (a) T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1949); (b) T. Moeller and G. L. King, *J. Am. Chem. Soc.*, **74**, 1355 (1952); (c) C. S. Patterson and S. Y. Tyree, Jr., *Ibid.*, **79**, 1828 (1957); (d) J. K. Ruff and S. Y. Tyree, Jr., *ibid.*, **80**, 5654 (1958); (e) H. R. Craig and S. Y. Tyree, Jr., *Inorg. Chem.*, **8**, 591 (1969).
(14) W. R. Harris and A. E. Martell, *Inorg. Chem.*, **15**, 713 (1976). These authors analyze their potentiometric titration data in terms of a 1/1 Ga citrate complex, whereas, the present study indicates that under the conditions of their experiments a complicated equilibrium exists between 1/1, 1/2 complexes and polymeric Ga citrate. Near neutral pH the 1/2 complex predominates. The composition of Ga citrate polymers proposed by these authors is also at variance with interpretations of NOE data in the present study.
(15) A. Einstein, "Investigations on the Theory of the Brownian Movement", Dover Publications, New York, N.Y., 1955.
(16) (a) T. G. Spiro, L. Pape, and P. Saltman, *J. Am. Chem. Soc.*, **89**, 5555 (1967); (b) T. G. Spiro, G. Bates, and P. Saltman, *ibid.*, **89**, 5559 (1967); (c) P. Saltman, *J. Chem. Educ.*, **42**, 682 (1965).
(17) B. Sarkar, *Can. J. Biochem.*, **48**, 1339 (1970).
(18) (a) O. E. Lanford and J. R. Quinan, *J. Am. Chem. Soc.*, **70**, 2900 (1948); (b) R. C. Warner and I. Weber, *ibid.*, **75**, 5086 (1953); (c) C. F. Timberlake, *J. Chem. Soc.*, 5075 (1964).
(19) M. Bobtelsky and J. Jordan, *J. Am. Chem. Soc.*, **69**, 2286 (1947).
(20) R. E. Blanco and J. D. Perkinson, *J. Am. Chem. Soc.*, **73**, 2696 (1951).
(21) J. P. Gallet and R. A. Paris, *Anal. Chim. Acta*, **39**, 341 (1967).
(22) R. A. Gams and J. D. Glickson, unpublished data.
(23) T. G. Spiro, S. E. Allertor, J. Renner, A. Terzis, R. Bils, and P. Saltman, *J. Am. Chem. Soc.*, **88**, 2721 (1966).

Nuclear Magnetic Resonance Studies of Metal Complexes Using Lanthanide Shift Reagents. Lanthanide-Induced Shifts in the ^1H (and ^{13}C) Spectra of Diamagnetic Metal Complexes of Quadridentate Ligands Incorporating Oxygen–Nitrogen Donor Atoms

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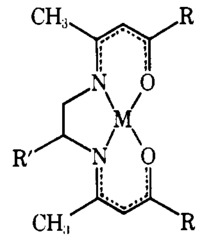
Abstract: Lanthanide shift reagents have been successfully used to induce shifts in the NMR spectra of a series of diamagnetic metal complexes of O_2N_2-donor quadridentate ligands; the ligands were prepared by condensation, in a 1:2 molar ratio, of ethylenediamine, propylenediamine, or 2,3-diaminobutane with a β-diketone. 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 results indicate that 1:1 adduct formation occurs with the lanthanide ion coordinated in a bidentate fashion to the cis-oxygen donor atoms of the respective metal complexes. The technique has formed the basis for a conformational study of the nickel(II) complex of the ligand obtained by 2:1 condensation of acetylacetone and propylenediamine. The results confirm a previous observation that the backbone methyl group in this complex occupies an axial position. An NMR investigation of the interaction of an optically active shift reagent with the above complex (as well as with the rac and meso isomers of the analogue derived from 2,3-diaminobutane) indicates that the technique can be extended to the study of suitable complexes which incorporate chiral centers. Apart from their intrinsic interest, these studies also demonstrate the suitability of certain classes of inorganic coordination complexes for examination by an NMR technique which has remained primarily in the hands of organic chemists.

Lanthanide shift reagents (LSRs)[1] such as $Eu(fod)_3$ have been routinely used to simplify the NMR spectra of organic[2,3] and, to a lesser extent, organometallic[4] compounds. However, provided suitably positioned heteroatoms are present in the ligands, LSRs may also be applied to the study of coordination compounds. This has been demonstrated previously for a few isolated complexes.[5]

As part of a general investigation of the use of LSRs to study bound organic ligands in diamagnetic coordination complexes, the effects of added shift reagent on the NMR spectra of metal complexes of type I have been studied. The complexes were chosen because they are diamagnetic, soluble in $CDCl_3$, and possess two oxygen donor atoms which have lone pair electrons available for further bonding to the LSR. Further, a considerable number of different compounds of this type are readily prepared and are thus available for comparative NMR studies. We now report an investigation of the effect of LSRs on the NMR spectra of a range of such complexes.



I

R	R'	Abbreviation
CH_3	H	M (Meaen)
CH_3	CH_3	M (Meapn)
C_2H_5	H	M (Etaen)
$i\text{-}C_3H_7$	H	M (*i*-Praen)
$i\text{-}C_4H_9$	H	M (*i*-Buaen)
$t\text{-}C_4H_9$	H	M (*t*-Buaen)
C_6H_5	H	M (Phaen)
CF_3	H	M (TFaen)

Experimental Section

Reagents and Handling Techniques. Eu(fod)$_3$, Pr(fod)$_3$, and Eu(dpm)$_3$ were obtained from Pierce Chemical Co; for each, the ^{1}H NMR spectra exhibited a sharp symmetrical peak for the tertiary butyl groups and no additional *tert*-butyl resonance appeared during the respective shift reagent runs. This is a reliable criterion of adequate purity for use of these reagents for quantitative measurements.[6] The optically active LSR, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), (+)Eu(fpc)$_3$, was obtained from Willow Brook Laboratories and was used as received.

Deuterated chloroform (CDCl$_3$) was obtained from Koch Light Laboratories and was stored over magnesium foil or freshly dried anhydrous sodium bicarbonate to remove any phosgene or hydrogen chloride.[7] The CDCl$_3$ was dried over Linde 3A molecular sieves for several days[7] before use in the experiments involving estimation of stability constants. For these studies the shift reagents were dried at 100 °C in vacuo over P_4O_{10} for 24 h before use to yield the anhydrous reagents.[8] All operations involving transfer of dry shift reagents were performed in a glove box filled with dry nitrogen. All glassware was preheated in an air oven and kept in a desiccator before use. For the quantitative measurements mentioned previously, the shift reagent runs were performed in the following manner. The substrate (metal complex) was dissolved in CDCl$_3$ (0.5 ml) in the NMR tube and LSR was then added directly (in a dry N$_2$ atmosphere). The NMR tube was capped and the solution was then mixed thoroughly; the spectrum was recorded after allowing 10 min for the solution to reach thermal equilibrium inside the NMR probe.

The ^{1}H NMR spectra were recorded at 100 MHz using a JEOL JNM-NH-100 spectrometer. The ^{13}C NMR were determined at Roche Research Institute of Marine Pharmacology (Sydney) using a JEOL JNM FX-60 spectrometer in the Fourier transform mode. Chemical shifts were measured relative to tetramethylsilane (TMS) as internal standard.

LSR-adduct formation constants were computed on a DEC-10 computer by an interactive (nonlinear least squares) procedure similar to that described elsewhere;[9] we thank Dr. K. Adam (James Cook University) for his help.

Preparation of the Compounds. The complexes Ni(Meaen), Ni(Meapn), Ni(Phaen), and Ni(TFaen) were prepared by published methods and their purity checked by ^{1}H NMR spectroscopy;[10] the melting points of all complexes agreed with the literature values. The preparation and characterization of other compounds of type I (including details of an x-ray structural determination on the compound with R = *t*-Bu, R′ = H) are described elsewhere.[11] All compounds were dried in vacuo over P_4O_{10} before use; all new compounds gave satisfactory elemental analyses.

4,9-Dimethyl-5,8-diazadodeca-3,9-diene-2,11-dionatoplatinum(II), Pt(Meaen), was prepared according to the published method,[10] mp 246 °C dec (lit.[10] 247 °C dec).

4,9-Dimethyl-5,8-diazadodeca-3,9-diene-2,11-dionatopalladium(II), Pd(Meaen), was also prepared by the published method,[10] mp 228 °C (lit.[10] 228 °C). The purity of both Pt(Meaen) and Pd(Meaen) was confirmed by their respective ^{1}H NMR spectra.[12]

4,9-Dimethyl-5,8-diazadodeca-3,9-diene-2,11-dithionatonickel(II), Ni(MeSaen), was prepared by the published method[13] and its purity was confirmed by means of its ^{1}H NMR spectrum.

4,9-Dimethyl-5,8-diazadodeca-3,9-diene-2,11-dithionatoplatinum(II), Pt(MeSaen), was prepared by a similar method to that used for the above compound. The ^{1}H NMR spectrum showed singlets at 6.02 (2 H, =CH—), 3.66 (4 H, -CH$_2$-), 2.12 (6 H, CH$_3$), and 1.92 ppm (6 H, CH$_3$). All peaks showed satellites resulting from coupling with ^{195}Pt; the $J_{\mathrm{Pt-H}}$ coupling constants were small (ca. 5–6 Hz) for all peaks except the diimine bridge proton resonance where $J \simeq 20$ Hz.

Preparation of Compounds Derived from Propylenediamine and 2,3-Diaminobutane. Optically pure *R*-propylenediamine was separated from *RS*-propylenediamine by the published method[14] and optically active Ni[Meapn] was prepared from it as outlined previously.[10] 2,3-Diaminobutane was obtained by reduction of butane-2,3-dione.[15] The meso and rac forms were separated as previously described[15] and the purity of their hydrochloride salts was confirmed by their respective ^{1}H NMR spectra.[16] The general procedure[10] was used to prepare the required meso and rac metal complexes.

Results and Discussion

The Nature of the Interaction. The ^{1}H NMR spectrum of Ni(Meaen) in deuteriochloroform has been previously described[12] and contains singlets at 1.87 (CH$_3$), 3.07 (-CH$_2$-), and 4.89 (=CH—) ppm. On successive additions of Eu(fod)$_3$ to a solution of this compound, the proton resonance shifts illustrated in Figure 1 occur. As is normally observed,[3] Eu(fod)$_3$ causes downfield shifts for each proton resonance and the relative magnitudes of the shifts suggest that the LSR interacts with the cis-oxygen atoms of the coordinated ligand.

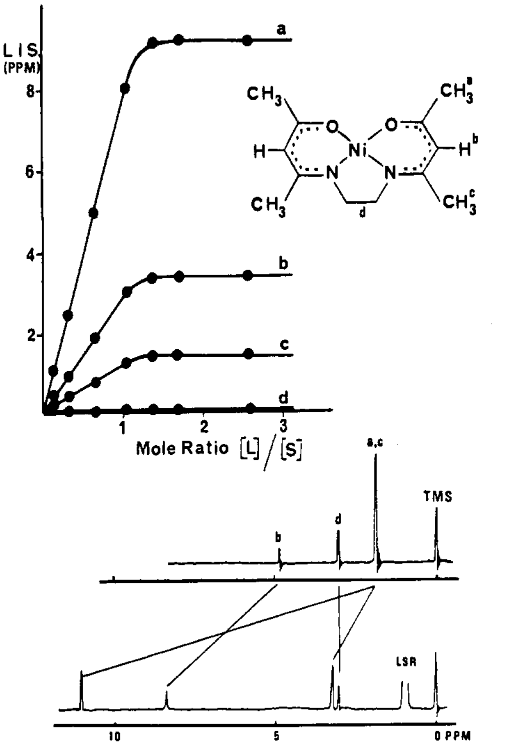
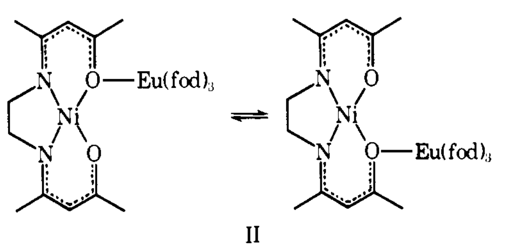
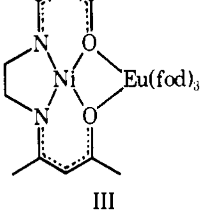


Figure 1. Lanthanide-induced shifts (LIS) induced by Eu(fod)$_3$ in the ^{1}H NMR spectrum of Ni(Meaen) in CDCl$_3$.

As the LSR is added, the original methyl peak (12 protons) at 1.87 ppm is split into two peaks (each of 6 protons) and one of these peaks undergoes a larger induced shift than any other resonance (Figure 1). This latter peak is thus assigned to the methyl groups nearest to the LSR.[17] Each resonance attains its limiting shift close to an LSR/substrate ratio of 1:1 and since no alteration of the shifts occurs when the ratio is much higher than 1:1 (Figure 1), this is evidence that the adduct formed between the complex and the LSR has a 1:1 stoichiometry.[6,18,19] Thus the interaction of the Eu(fod)$_3$ with the nickel complex could either be monodentate and of type II or bidentate and of type III. The possibility that the interaction



II



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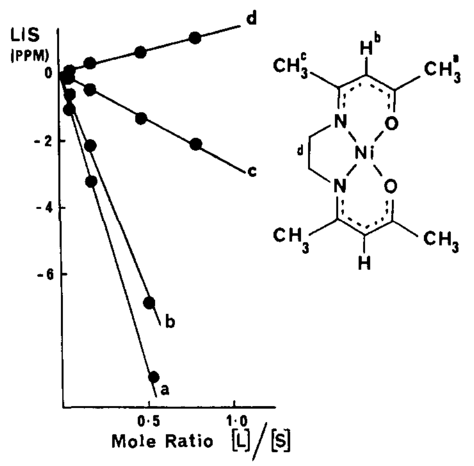


Figure 2. Lanthanide-induced shifts (LIS) induced by Pr(fod)$_3$ in the ^{1}H NMR spectrum of Ni(Meaen) in CDCl$_3$.

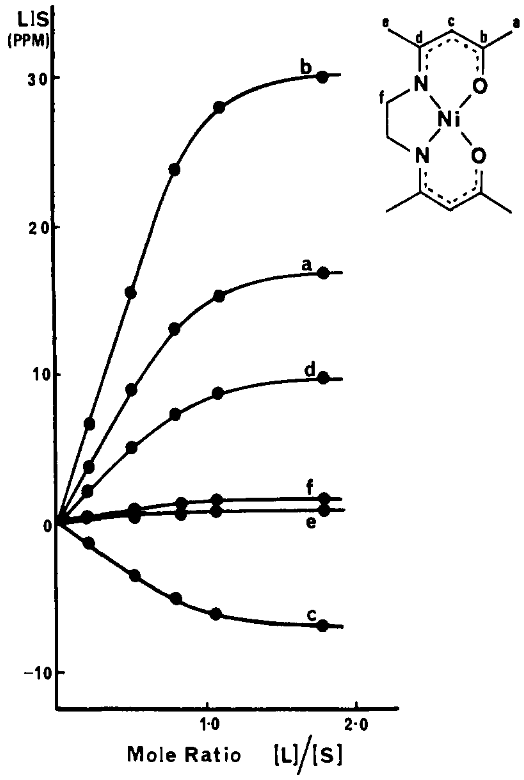


Figure 3. Lanthanide-induced shifts (LIS) induced by Eu(fod)$_3$ in the ^{13}C NMR spectrum of Ni(Meaen) in CDCl$_3$.

is monodentate and is associated with a rapid equilibrium between the oxygen donor sites on the nickel complex, as seen in II, cannot be dismissed on the present evidence. Nevertheless, the ability of europium (and of the other lanthanide ions) to expand its coordination number from six to eight has been well documented,[20-23] and the lone pair electrons associated with such cis-oxygen donors in related complexes have been shown to be capable of coordinating simultaneously to a second metal ion.[24-26] Examples of bifunctional organic molecules acting as bidentate ligands toward LSRs are also known.[27-31] It is also pertinent that both Eu(fod)$_3$ and Pr(fod)$_3$ have been shown to self-associate (in CCl$_4$) via bridging β-diketone oxygen donors in a manner which appears quite similar to the reaction proposed here.[19] In view of the above evidence it seems likely that structure III represents the most plausible model for the present interaction. Indeed, the relatively large formation constants found for the complex-LSR adducts (see later) may reflect the operation of the chelate effect which should occur for an interaction of type III.

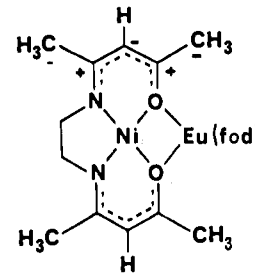


Figure 4. The possible result of contact contributions on the induced shifts in the NMR spectrum of Ni(Meaen) in the presence of Eu(fod)$_3$: + indicates a contact shift parallel to the normal pseudo-contact shift direction and – indicates that it is in the opposite direction.

The lanthanide-induced shifts of the various protons are readily interpreted in terms of structure III; however, although a general trend of diminution of shift with distance from the LSR is apparent (Figure 1), a detailed analysis of the magnitude of the shifts associated with bidentate systems of this type appears not appropriate[31,32] in terms of the unusual McConnell-Robertson equation.[33]

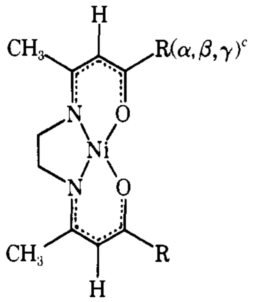
The interaction of Pr(fod)$_3$ with Ni(Meaen) (Figure 2) differs from the interaction of Eu(fod)$_3$ with this complex in two respects. First, as is usually found for Pr(fod)$_3$,[4,5] most of the proton signals of the substrate experience upfield shifts. Second, the shifts are in general significantly larger than those found with Eu(fod)$_3$.

With Pr(fod)$_3$, the protons of the chelate ring derived from ethylenediamine in Ni(Meaen) experience a downfield shift (Figure 2). This phenomenon of specific signals being shifted in an opposite direction to that normally observed has been well documented previously[34,35] and in some instances has been postulated to arise from a change in sign of the angular term of the McConnell-Robertson equation.[33] However, in other systems an observed reversal of shift direction has been attributed to the presence of significant contact interaction.[1,35-38]

In order to investigate further the possibility that a contact shift component contributes to the observed spectral shifts, the ^{13}C NMR spectrum of Ni(Meaen)[39] in the presence of increasing amounts of Eu(fod)$_3$ was recorded (Figure 3); it has been documented that contact interactions tend to contribute more readily to ^{13}C NMR shifts than to ^{1}H shifts.[40] The possible result of any contact shift contribution on the spectrum of Ni(Meaen) (after adduct formation with Eu(fod)$_3$) is shown in Figure 4; the resonances of only three of the different carbon types present may be influenced by contact terms which oppose the usual direction of the pseudo-contact shift. Two of these carbon atoms (the two methyl carbons) are not directly part of the π system and so should be less affected by contact interactions. Indeed, it is found that the resonances of both of these carbons show normal downfield shifts in the presence of Eu(fod)$_3$ (Figure 3). In contrast, the central carbon of the chelate ring derived from acetylacetone may experience a contact interaction which opposes the normal pseudo-contact interaction (Figure 4). In this case the contact shift would be expected to be significant since this carbon does form part of the π system. The opposite lanthanide-induced shift of this carbon (Figure 3) thus provides reasonable evidence that a contact contribution does operate in this system.

If the above model for the interaction of the LSR with Ni(Meaen) is correct then a reduction of the induced shifts should occur if the steric crowding around the donor site of the substrate is increased by the presence of bulky substituents. A list of analogues of Ni(Meaen) which are derived from various

Table I. ^{1}H NMR Spectral Shifts for Nickel(II) Complexes of the Type Ni(Raen) in the Presence of Eu(fod)$_3$[a]



Compd	R	Limiting shifts α	β	γ	=CH—	CH$_3$	-CH$_2$-
Ni(Meaen)	Me	9.3			3.4	1.5	0.1
Ni(Etaen)	Et	7.5	2.0		3.2	1.4	0.1
Ni(*i*-Praen)	*i*-Pr	0.3	1.4		2.9	1.4	0.4
Ni(*i*-Buaen)	*i*-Bu	0.2	*b*	0.9	2.8	1.3	0.2
Ni(*t*-Buaen)	*t*-Bu		0.1		0.08	0.03	0.04
Ni(Phaen)	Ph				Small shifts, see text		
Ni(TFaen)	CF$_3$				No observed change		

[a] In ppm downfield; ~1 M solutions in CDCl$_3$ at 32 °C. [b] Resonance too broad and complex to allow resolution. [c] Where α designates the protons on the carbon α to the C=O group etc.

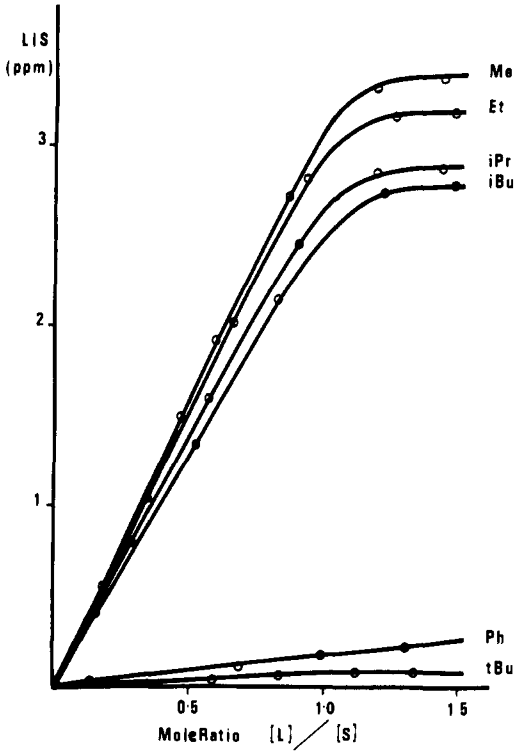


Figure 5. Comparison of the relative Eu(fod)$_3$-induced shifts of the central protons of the O-N donor chelate rings in complexes of type Ni(Raen) with change of R.

nonsymmetric β-diketones is given in Table I. All of these complexes have been shown by NMR and mass spectral data [as well as an x-ray structural determination for Ni(*t*-Buaen)] to have the structure indicated[11] (see Table I); their behavior in the presence of Eu(fod)$_3$ is also summarized in Table I.

The behavior of Ni(Etaen) with Eu(fod)$_3$ (Table I) is very similar to that of the parent compound, although the change from methyl to ethyl results in slightly smaller induced shifts for all protons of Ni(Etaen). The reduction in the induced shifts becomes increasingly evident for the complexes containing more bulky substituents. The order of the observed induced shifts was Me > Et > *i*-Pr > *i*-Bu ≫ Ph > *t*-Bu and strongly implies that a steric factor is operating,[41] although concomitant electronic changes may also influence the shifts (see later).

Table II. Summary of Eu(fod)$_3$-Induced ^{1}H NMR Spectral Shifts for Nickel, Palladium, and Platinum Complexes of Type M(Meaen)

Compd	Limiting Shifts[a] CH$_3$(O)	CH$_3$(N)	=CH—	-CH$_2$-
Ni(Meaen)	9.3	3.4	1.5	0.1
Pd(Meaen)	14.8	3.2	1.8	1.2
Pt(Meaen)	11.9	3.8	2.2	1.7

[a] In ppm; ~1 M solutions in CDCl$_3$ at 32 °C.

Figure 5 summarizes the observed shifts for the central proton of each β-diketone-derived chelate ring as increasing amounts of Eu(fod)$_3$ are added.

The importance of steric factors in influencing the induced shifts is further seen for the most hindered species Ni(*t*-Buaen) for which only negligible shifts were observed for all protons.[42]

The small shifts experienced for Ni(Phaen) when Eu(fod)$_3$ is added may also be a reflection of steric hindrance of the type discussed above, although in this case electronic effects could also strongly influence the magnitude of the observed shifts. The decreased lanthanide-induced shifts may reflect removal of electron density by the substituent benzene rings which thus make the donor oxygens poorer Lewis bases toward Eu(fod)$_3$.

To investigate the influence of electronic factors, the complex Ni(TFaen) (see Table I) was prepared since the relatively small CF$_3$ group should withdraw electron density from the conjugated chelate ring and reduce the capacity of the oxygen donors to coordinate simultaneously to the LSR. Accordingly, no evidence for adduct formation was observed on addition of Eu(fod)$_3$ to this complex in CDCl$_3$.[43]

The interaction of Eu(fod)$_3$ with other (d^8) square-planar complexes of type M(Meaen), where M = Pd or Pt, has also been studied. The observed spectral shifts are listed in Table II as are the values for Ni(Meaen). It would be expected that the extent of electron delocalization will differ in the three complexes. The larger 5d orbitals of platinum and 4d orbitals of palladium should overlap to a greater extent with the ligand orbitals and hence a greater degree of electron delocalization is expected in these metal complexes.

Any change in the electronic distribution of the ligand system will be reflected by a change in the contact shift contri-

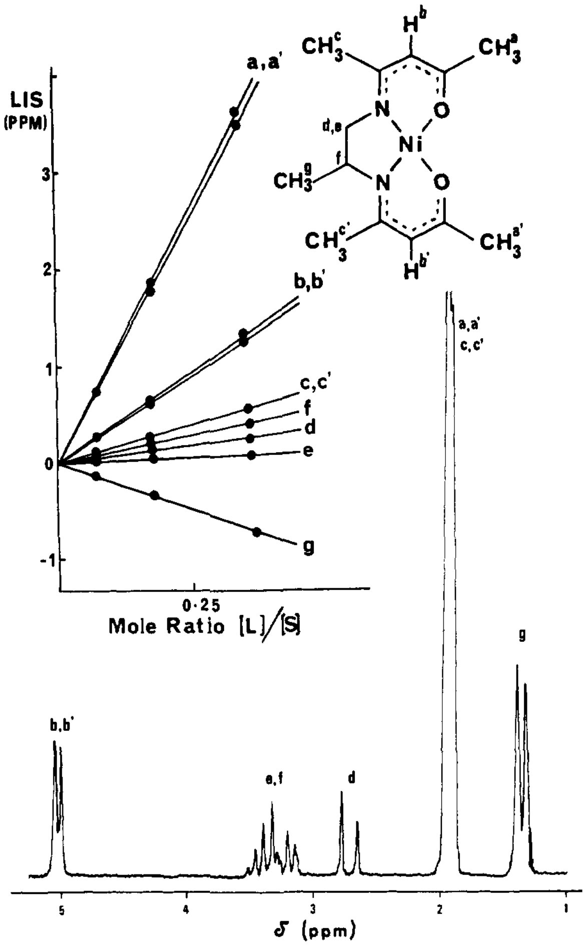


Figure 6. ^{1}H NMR spectrum (100-MHz) of Ni(Meapn) (in $CDCl_3$) together with the effects of addition of $Eu(fod)_3$ on the chemical shifts of the respective resonances.

Table III. Values for Adduct Formation Constants[a]

Compd	K, M^{-1} [$Eu(fod)_3$[b]]
Ni(Meaen)	>1000
Pd(Meaen)	900 ± 400[c]
Pt(Meaen)	500 ± 200
Ni(*i*-Praen)	600 ± 200

[a] At 32 °C for ~0.1 M solutions in $CDCl_3$. [b] Solvent, complex, and LSR rigorously dried (see Experimental Section). When undried solvent and reagents were used, significantly lower K values were observed in each case owing to competition of water for the LSR. [c] Assessed error.

bution. As the delocalization increases, the contact shift should increase. Since the protons of the acetylacetone-derived rings of the ligand might be expected to show contact shift contributions in the same direction as the pseudocontact shift, it would be predicted that these proton resonances for the platinum and palladium complexes could experience larger downfield shifts than are found for the nickel complex. With one exception this is as observed (Table II).[44]

Variation of the metal ion would also be expected to alter the respective formation constants for adduct formation with $Eu(fod)_3$. Because of the greater electron delocalization when the metal is changed from nickel to palladium or platinum, the oxygen donor atoms may become "softer" and thus be expected to bind less strongly to the "hard" europium ion. Consequently, the value of the adduct formation constant (K) might be expected to decrease in the order $K_{Ni} > K_{Pd} > K_{Pt}$.

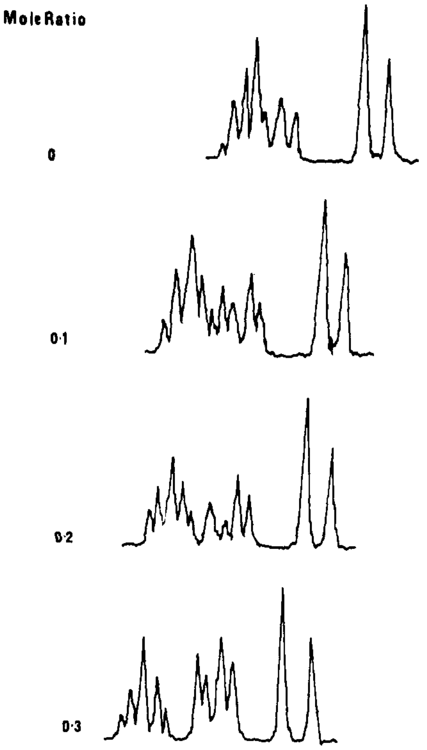


Figure 7. Changes in the 2.5–4.0-ppm region of the ^{1}H NMR spectrum of Ni(Meapn) on successive additions of $Eu(fod)_3$.

Table III lists numerical estimates of K computed from the respective lanthanide-induced shifts vs. mole ratio plots. Because of experimental limitations in their determination, the K values are not of high accuracy; nevertheless, the values do suggest the above order.[45]

For comparison, the estimated value of the adduct formation constant for Ni(*i*-Praen) is also included in Table III. As expected, the presence of the bulky isopropyl group in the vicinity of the donor site results in a significant lowering of the constant relative to the value for Ni(Meaen).

Conformational Studies Involving $Eu(fod)_3$. In an attempt to extend the LSR study to conformational aspects of a selected inorganic complex, the spectrum of Ni(Meapn) (I: $R' = CH_3$, $R = CH_3$, $X = H$) was examined in the presence of varying amounts of $Eu(fod)_3$. The 100-MHz ^{1}H-NMR spectrum of this compound is shown in Figure 6. Except for the multiplet which arises from the diimine bridge protons (i.e., H_d, H_e, and H_f), the assignment of the spectrum is straightforward; the assignments given agree with those reported previously for this complex.[12,46]

The changes which occur in the part of the spectrum arising from the diimine bridge (viz., the multiplet extending from 2.5 to 3.5 ppm) on addition of successive amounts of $Eu(fod)_3$ are shown in Figure 7. It is evident that the original multiplet separates into three distinct signals, namely, a doublet, a doublet of doublets, and a five-peak signal. The doublet is assigned to the signal arising from H_d and the coupling constant of 12.8 Hz (which is characteristic of a geminal coupling constant) is taken as being J_{de}. Since this signal is a doublet there can be essentially no coupling of H_d to the remaining proton H_f and consequently J_{df} is taken as zero (see later). The doublet of doublets can be assigned to H_e since this is the expected signal complexity for a proton coupled to two other nonequivalent protons (i.e., H_d and H_f).

Based on the above assignments the coupling constant, J_{ef}, can be estimated to be 5.6 Hz. Thus the remaining five-peak signal can be assigned to H_f and its multiplicity arises from it being coupled to the methyl group protons (H_g) and also to H_e.

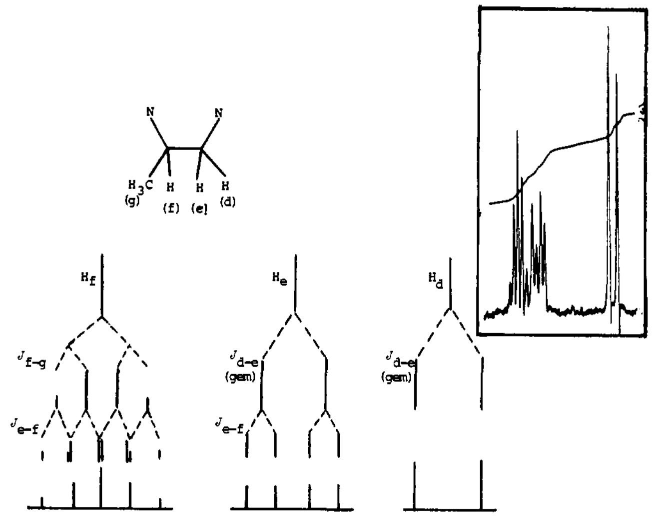


Figure 8. Postulated first-order NMR coupling scheme for diamine backbone of Ni(Meapn). Insert: observed spectrum at 220 MHz.

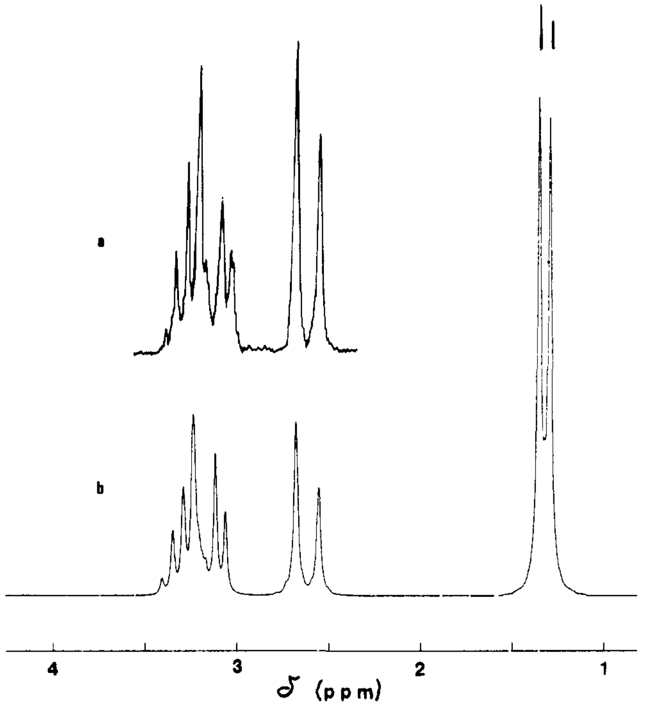
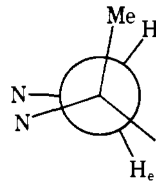


Figure 9. (a) Observed 100-MHz spectrum of Ni(Meapn); (b) computer-simulated spectrum.

The value 6.2 Hz for J_{fg} is readily available from the splitting of the methyl signal. A summary of the proposed (first order) coupling scheme is given in Figure 8.

For comparison with the expanded 100-MHz spectrum obtained on addition of Eu(fod)$_3$, the spectrum of Ni(Meapn) was run at 220 MHz in the absence of Eu(fod)$_3$. In agreement with the results from the shift reagent study, a similar spectral pattern for the backbone resonances (cf. Figure 7) was obtained at this higher frequency; the relevant portion of the 220-MHz spectrum is reproduced in Figure 8.

Thus by use of Eu(fod)$_3$ to expand the spectrum it has been possible to obtain estimates of the four coupling constants involved in the part of the spectrum derived from the diimine backbone. In order to confirm the above assignments the relevant portion of the spectrum (in the absence of LSR) was simulated by means of the LAOCN III computer program using the coupling constants determined from the lanthanide-shifted spectrum. It is assumed in this approach that the observed coupling constants for the substrate-LSR adduct remain unchanged from those for the free substrate. Although this is often the case,[47] it is not necessarily true for all cases.[48] The chemical shifts were obtained by extrapolation of the appropriate chemical shifts in the expanded spectrum to values at zero concentration of Eu(fod)$_3$. The results of the computer simulation are shown in Figure 9; excellent agreement is found between the experimentally observed and the simulated spectra. The present assignments are in good agreement with those from a previously reported NMR study of this complex based on the INDOR technique.[46] The authors of this study also concluded that the value of J_{df} was close to zero and, by application of the Karplus equation,[49] postulated the dihedral angle for H$_d$–H$_f$ to be ca. 90°. They further postulated that this value could occur only if the conformation of the chelate ring derived from propylenediamine in Ni(Meapn) is such that the methyl group substituent occupies an axial position. The postulated[46] Newman projection along the backbone C–C bond of Ni(Meapn) is given below:



The results of the present LSR study of Ni(Meapn) are thus in complete accord with the findings of the above earlier study[46] and support the conclusion that the methyl group of the chelate ring derived from propylenediamine occupies an axial position.[50]

Investigations Involving an Optically Active LSR. In the presence of optically active LSRs, the spectra of both chiral and achiral substrates will show the normal induced shifts

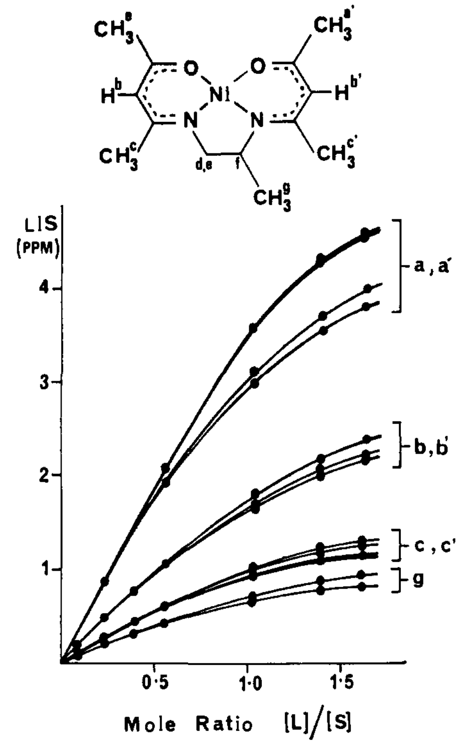


Figure 10. Lanthanide-induced shifts in the ^{1}H NMR spectrum of a racemic mixture of Ni(Meapn) in CDCl$_3$ in the presence of (+)Eu(fpc)$_3$. (The signals arising from the protons d, e, f are obscured by the resonances of the LSR.)

Table IV. ^{1}H NMR Spectral Assignments for Ni(Meabn)[a]

Compd	Assignment CH_3—CH	 CH_3—C	 CH_3—CH	 =CH—
rac-Ni(Meabn)	1.28, doublet, J = 6 Hz (−0.45)[b]	1.85 (O), 1.88 (N), singlets (13.40) (1.45)	2.85, quartet J = 6 Hz (0.78)	4.88, singlet (3.60)
meso-Ni(Meabn)	1.35, doublet, J = 6 Hz (−0.67)	1.85 (O), 1.89 (N), singlets (6.75) (2.08)	3.38, quartet[c] (2.20)	4.89, singlet (2.35)

[a] In ppm downfield from TMS as internal standard; ~10^{-1} M solutions in $CDCl_3$ at 32 °C. [b] Induced shifts in the presence of excess $Eu(fod)_3$ are shown in parentheses. [c] This signal is poorly resolved.

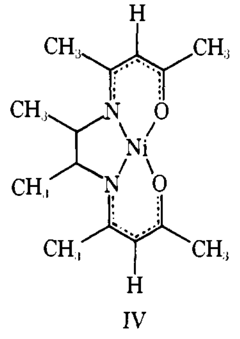
which result from interaction with the paramagnetic lanthanide ion. However, for a chiral substrate, the spectrum will also show a difference in the induced shifts of the respective nuclei of each enantiomer present, this difference resulting from the formation of diastereomeric adducts.[51]

Such behavior is demonstrated by the spectrum of a racemic mixture of Ni(Meapn) in the presence of (+)$Eu(fpc)_3$ (Figure 10).

The two chiral forms, *R*-Ni(Meapn) and *S*-Ni(Meapn), result from the presence of an asymmetric carbon in the chelate ring derived from propylenediamine. The two diastereomeric adducts with (+)$Eu(fpc)_3$ will each have its own formation constant[52] and geometry.[3] Consequently, as observed (Figure 10), the NMR spectrum for the racemic substrate in the presence of (+)$Eu(fpc)_3$ would be expected to be a composite of two overlapping, nonequivalent spectra (and could contain up to twice as many peaks as the spectrum obtained in the presence of an achiral LSR).[53,54]

In a similar manner a compound containing two asymmetric centers (which are not equivalent) will give rise to four overlapping spectra (excluding any effects which result from conformational isomers) in the presence of a chiral LSR. In this case, the intensity of each individual spectrum will depend on the proportion of each stereoisomer present.

A special case arises when the asymmetric atoms are chemically equivalent as, for example, are the two asymmetric carbon atoms in the chelate ring derived from 2,3-diaminobutane in Ni(Meabn) (IV). For this compound, the diamine backbone gives rise to two forms (meso and rac) which are chemically different and hence each should be NMR observable. By initial separation of 2,3-diaminobutane into meso and rac forms, the corresponding forms of Ni(Meabn) were prepared and the ^{1}H NMR spectrum of each was obtained. The assignments for each are listed in Table IV.



IV

On addition of $Eu(fod)_3$, both isomers behave in a similar manner to that found for related complexes discussed previously and the observed limiting shifts of the various proton resonances are given in parentheses in Table IV.

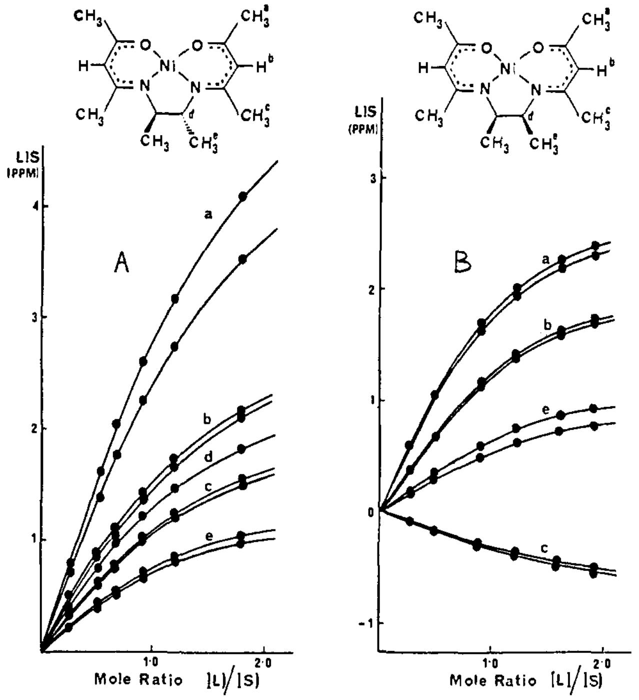


Figure 11. The effect of (+)$Eu(fpc)_3$ on the ^{1}H NMR spectrum of (A) *rac*-Ni(Meabn) and (B) *meso*-Ni(Meabn) ($CDCl_3$ as solvent).

The ^{1}H NMR spectral behavior of these complexes was also examined in the presence of (+)$Eu(fpc)_3$. The changes in the spectrum of *rac*-Ni(Meabn) on incremental addition of (+)-$Eu(fpc)_3$ are illustrated graphically in Figure 11; the spectrum now shows the expected two sets of spectral peaks, one set for the *R,R*-Ni(Meabn)-(+)$Eu(fpc)_3$ diastereomer and the other for the *S,S*-Ni(Meabn)-(+)$Eu(fpc)_3$ diastereomer.

The behavior of *meso*-Ni(Meabn) in the presence of (+)-$Eu(fpc)_3$ is slightly more complex. The (+)$Eu(fpc)_3$-induced spectral changes for this isomer are also shown in Figure 11, from which it may be seen that this nonoptically active compound also yields two overlapping sets of spectral peaks. In this case the two sets cannot result from two distinct diastereomers because the substrate is achiral; rather the observed behavior results from the presence of a meso plane[55] which bisects the carbon-carbon bond of the chelate ring derived from butanediamine and renders both halves of the molecule enantiotropic. The chiral LSR thus affects the two halves of the molecule differently and hence two sets of spectral peaks are observed. This phenomenon has been demonstrated to occur in the spectra of some organic compounds containing prochiral centers on addition of chiral LSRs[56,57] and has been used to distinguish between meso and rac structures.[57]

Acknowledgment. We thank the Australian Research Grants Committee for support.

References and Notes

(1) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, N.Y., 1973.
(2) J. K. M. Sanders and D. H. Williams, *Nature (London)*, **240**, 385 (1972); B. C. Mayo, *Chem. Soc. Rev.*, **2**, 49 (1972).

(3) J. Reuben, *Prog. Nucl. Magn. Reson. Spectroscopy*, **9**, 3 (1973); A. F. Cockerill, G. L. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).

(4) See, for example, M. I. Foreman and D. G. Leppard, *J. Organomet. Chem.*, **31**, C31 (1971); T. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, *ibid.*, **33**, C35 (1971); M. Gielen, N. Goffin, and J. Topart, *ibid.*, **32**, C38 (1971); J. Paul, K. Schlogl, and W. Silhan, *Monatsh. Chem.*, **103**, 243 (1972); B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J. Chem. Soc., Dalton Trans.*, 1253 (1974); D. L. Reger, *Inorg. Chem.*, **14**, 660 (1975); R. S. Dickson, S. H. Johnson, and I. D. Rae, *Aust. J. Chem.*, **28**, 1681 (1975).

(5) G. R. Tauszik, G. Pellizer, and G. Costa, *Inorg. Nucl. Chem. Lett.*, **9**, 717 (1973); M. Nonoyama, K. Sato, and K. Yamasaki, *Nippon Kagaku Kaishi*, 695 (1974); S. J. Anderson and A. H. Norbury, *J. Chem. Soc., Chem. Commun.*, 48 (1975); L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, **97**, 2275 (1975); L. F. Lindoy, H. W. Louie, and W. E. Moody, Abstract, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., August, 1976; A. R. Hendrickson, J. M. Hope, and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 2032 (1976).

(6) M. D. Johnston, Jr., B. L. Shapiro, M. J. Shapiro, T. W. Proulx, A. D. Godwin, and H. L. Pearce, *J. Am. Chem. Soc.*, **97**, 542 (1975).

(7) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

(8) C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967); A. H. Bruder, S. R. Tanny, H. A. Rockefeller, and C. S. Springer, *ibid.*, **13**, 880 (1974).

(9) W. M. Wang and N. C. Li, *J. Am. Chem. Soc.*, **90**, 5069 (1968).

(10) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955); R. H. Holm, *ibid.*, **82**, 5632 (1960); L. F. Lindoy, H. C. Lip, and W. E. Moody, *J. Chem. Soc., Dalton Trans.*, 44 (1974).

(11) L. F. Lindoy, W. E. Moody, and D. Taylor, *Inorg. Chem.*, accepted for publication: mass spectral, NMR (^{1}H and ^{13}C), and x-ray structural data confirm that the compounds of type I have the structure indicated.

(12) P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, **6**, 781 (1967).

(13) R. M. C. Wei and S. C. Cummings, *Inorg. Nucl. Chem. Lett.*, **9**, 43 (1973).

(14) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

(15) F. J. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

(16) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1707 (1964).

(17) The line width of this peak broadens as the peak shifts then narrows as the limiting shift is approached. This behavior provides a textbook example of the nondilute case of fast exchange NMR line broadening. See J. K. Beattie, L. F. Lindoy, and W. E. Moody, *Inorg. Chem.*, **15**, 3170 (1976).

(18) R. Porter, T. J. Marks, and D. F. Shriver, *J. Am. Chem. Soc.*, **95**, 3548 (1973); J. W. Apsimon, H. Beierbeck, and A. Fruchier, *ibid.*, **95**, 939 (1973); B. L. Shapiro and M. D. Johnston, *J. Am. Chem. Soc.*, **94**, 8185 (1972).

(19) A. H. Bruder, S. R. Tanny, H. A. Rockefeller, and C. S. Springer, *Inorg. Chem.*, **13**, 880 (1974).

(20) R. G. Charles and R. C. Ohlmann, *J. Inorg. Nucl. Chem.*, **27**, 119 (1965).

(21) J. E. Schwarberg, D. R. Gere, R. E. Sievers, and K. J. Eisentraut, *Inorg. Chem.*, **6**, 1933 (1967).

(22) R. E. Cramer and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).

(23) J. H. Frosberg, *Coord. Chem. Rev.*, **10**, 195 (1973); P. Glentworth, A. L. Nichols, D. A. Newton, N. R. Large, and R. J. Bullock, *J. Chem. Soc., Dalton Trans.*, 546 (1973); S. J. Lyle and A. D. Witts, *ibid.*, 185 (1975).

(24) Adducts of this type are known in which the second metal ion is a transition metal ion such as copper (ref 25) or an alkali metal ion such as sodium (ref 26). This second adduct type is of particular relevance since the oxygen–sodium bonds will be essentially electrostatic and hence related to the bond type postulated to occur between lanthanide ions and a range of organic substrates.

(25) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).

(26) L. G. Armstrong, L. F. Lindoy, H. C. Lip, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, accepted for publication. The structure of the adduct [Ni(Meaen)]$_2$·NaClO$_4$ has been determined by x-ray diffraction and each Ni(Meaen) molecule is bonded to the sodium ion in a bidentate fashion via cis-oxygen atoms.

(27) A study of the Eu(fod)$_3$ induced shifts in the spectra of a series of methoxybenzenes has shown that chelation to the Eu(fod)$_3$ can have a large effect on the magnitude of the induced shifts; see ref 32.

(28) G. E. Wright and T. Y. Tang Wei, *Tetrahedron*, 3775 (1973).

(29) A. M. Grotens, J. Smid, and E. de Boer, *Tetrahedron Lett.*, 4863 (1971).

(30) A. M. Grotens, G. W. Hilbers, and E. de Boer, *Tetrahedron Lett.*, 2067 (1972); A. M. Grotens, J. J. Backus, and E. de Boer, *ibid.*, 1465 (1973).

(31) N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Am. Chem. Soc.*, **94**, 8719 (1972).

(32) O. Ceder and B. Beijer, *Acta Chem. Scand.*, 26, 2977 (1972).

(33) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(34) B. L. Shapiro, J. R. Klubucek, G. R. Sullivan, and L. F. Johnson, *J. Am. Chem. Soc.*, **93**, 3281 (1971); P. H. Mazzocchi, H. J. Tamburin, and G. R. Miller, *Tetrahedron Lett.*, 819 (1971); R. E. Rondeau, M. A. Berwick, R. N. Steppel, and M. P. Serve, *J. Am. Chem. Soc.*, **94**, 1096 (1972); M. Kishi, K. Tori, and T. Komono, *Tetrahedron Lett.*, 3525 (1971); W. R. Willcott, J. F. Oth, J. Thio, G. Plinke, and G. Schroder, *ibid.*, 1579 (1971); T. H. Siddall, *J. Chem. Soc., Chem. Commun.*, 452 (1971).

(35) R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *J. Chem. Soc., Chem. Commun.*, 636 (1972).

(36) For studies involving lanthanide shift reagents contact shifts have often been thought to be of little importance in comparison to pseudo-contact shifts; nevertheless, this is not always so and contact shifts may be of considerable importance in compounds containing extended π systems as well as for the signals of those atoms which are close to the site of attachment of the LSR (see ref 3 and 28).

(37) J. Reuben and J. S. Leigh, *J. Am. Chem. Soc.*, **94**, 2789 (1972).

(38) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Am. Chem. Soc.*, **94**, 5325 (1972); F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970); E. R. Birnbaum and T. Moeller, *J. Am. Chem. Soc.*, **91**, 7274 (1969); K. Tori and Y. Yoshimura, *Tetrahedron Lett.*, 1573 (1973).

(39) L. F. Lindoy, W. E. Moody, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Dalton Trans.*, 1965 (1976).

(40) R. E. Davis and M. R. Willcott in ref 1; G. E. Hawkes, D. Liebfritz, D. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 1659 (1973); D. Doddrell and J. D. Roberts, *ibid.*, **92**, 6839 (1970); A. A. Chalmers and K. G. R. Pachler, *Tetrahedron Lett.*, 4033 (1972); M. Hirayama, E. Edagawa, and Y. Hanyo, *J. Chem. Soc., Chem. Commun.*, 1343 (1972); D. J. Chadwick and D. H. Williams, *ibid.*, 128 (1974).

(41) The large decreases in the lanthanide-induced shifts of the α protons of the respective R groups in going from ethyl to isopropyl or isobutyl may be indicative of a change in the conformation of these latter two R groups on adduct formation. In these compounds, the R group protons form part of a flexible aliphatic chain and with the approach of the large Eu(fod)$_3$ molecule steric repulsions may alter the positions of these aliphatic chains. The unexpectedly small shifts experienced by the α protons may thus reflect that the side chains adopt a new conformation for which the distance and angle terms (for the α protons) result in only small lanthanide-induced shifts.

(42) The ^{1}H NMR spectrum of Ni(Meaen) was also examined in the presence of Eu(dpm)$_3$; this LSR is more bulky than Eu(fod)$_3$. Owing to the low solubility of Eu(dpm)$_3$ it was not possible to obtain the complete lanthanide-induced shift vs. mole ratio plot and limiting shifts could not be determined. Nevertheless it was evident from the curves that the LSR-induced shifts are considerably smaller than those with Eu(fod)$_3$. The lower shifting ability of Eu(dpm)$_3$ may be a reflection of its greater size yielding increased steric repulsion of the substrate and a concomitant increase in the substrate–Eu bond distances. Alternatively the known lower Lewis acidity of this LSR may simply result (primarily because of different electronic influences) in both a different geometry for the adduct as well as a change in the nature of the pseudo-contact and contact interactions which operate.

(43) In order to investigate further the influence of electronic factors, the effects of Eu(fod)$_3$ on the NMR spectra of complexes of type I ($R' = H$, $R = CH_3$ but with the central β-diketone carbons substituted by CH$_3$, Cl, Br, I, or C$_6$H$_5$S) have been studied. In each case a marked decrease was observed in the limiting shift of the methyl protons which are adjacent to the oxygen donors, while the limiting shifts of the other methyl protons and of the diamine-derived backbone was slightly increased. Since both electron-withdrawing and electron-donating substituents were found to cause somewhat similar changes in the induced shifts, it appears that electronic factors alone are not sufficient to explain the observed behavior.

(44) A second result of a change in the electron delocalization would be to alter the electronic properties of the oxygen donor atoms and hence also the nature of the O–Eu bonds. As a consequence of this both the contact and pseudo-contact contributions will be different in the three complex–LSR adducts.

(45) For comparison with their oxygen donor analogues, the disulfur complexes [Ni(MeSaen)] and [Pt(MeSaen)] were prepared and their spectra were examined in the presence of Eu(fod)$_3$ and Eu(dpm)$_3$. Neither spectrum showed any change on addition of these LSRs. This is very likely the result of the presence of "softer" sulfur atoms; as mentioned in the text, LSRs have been well documented to prefer "hard" donor atoms. See: T. C. Morrill, R. A. Clark, D. Bilobran, and D. S. Young, *Tetrahedron Lett.*, 397 (1975); A. Van Bruijnsvoort, C. Kruk, E. R. De Waard, and H. O. Huisman, *ibid.*, 1737 (1972); T. C. Morrill, R. J. Opitz, and R. Mozzer, *ibid.*, 3715 (1973); J. Campbell, *Aldrichimica Acta*, **4**, 55 (1971); I. D. Rae, *Aust. J. Chem.*, **28**, 2527 (1975).

(46) E. Larsen and K. Schaumberg, *Acta Chem. Scand.*, **25**, 962 (1971).

(47) J. A. Peters, J. D. Remijnse, A. Van de Wiele, and H. Van Bekkum, *Tetrahedron Lett.*, 3065 (1971); F. I. Carroll and J. T. Blackwell, *ibid.*, 4173 (1970); A. F. Bramwell, G. Riezebos, and R. D. Wells, *ibid.*, 2489 (1971).

(48) B. L. Shaprio, M. D. Johnston, and R. L. R. Towns, *J. Am. Chem. Soc.*, **94**, 4381 (1972); K. T. Liu, *Tetrahedron Lett.*, 5039 (1972); T. B. Patrick and P. H. Patrick, *J. Am. Chem. Soc.*, **94**, 6230 (1972); W. G. Bentrude, H. W. Tan, and K. C. Yee, *ibid.*, **94**, 3264 (1972).

(49) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(50) A recent x-ray structural study of Cu(Meapn) indicates that the methyl group of the propylenediamine-derived ring does occupy an axial position: E. Larsen, S. Larsen, S. Røen, and K. J. Watson, *Acta Chem. Scand.*, **30**, 125 (1976).

(51) C. Kutal, "Nuclear Magnetic Resonance Shift Reagents", R. E. Sievers, Ed., Academic Press, New York, N.Y., 1973.

(52) G. M. Whitesides and D. W. Lewis, *J. Am. Chem. Soc.*, **92**, 6979 (1970).

(53) For racemic Ni(Meapn), not all of the resonances are resolved into two separate signals (Figure 10). For example, for the protons designated a and a' in Figure 10, only three of the expected four signals are observed; however one of these signals has an intensity which is twice that of each of the remaining two signals and clearly results from an accidental chemical shift equivalence of two signals.

(54) Addition of (+)Eu(fpc)$_3$ to *R*-Ni(Meapn), prepared directly from *R*-propylenediamine, yielded the expected single set of resonances in the NMR spectrum. By comparison of the lanthanide-induced shift vs. mole ratio plot for this case with that shown in Figure 10, it is thus possible to assign specific resonances in the latter to either the *R* or *S* forms of the complex.

(55) E. L. Eliel, Ed., "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 10 and 27; M. Raban and K. Mislow, *Top. Stereochem.*, **1**, 1 (1967).

(56) R. R. Fraser, M. A. Petit, and M. Miskow, *J. Am. Chem. Soc.*, **94**, 3253 (1972).

(57) M. Kainosho, K. Ajisaka, W. H. Pirkle, and S. D. Beare, *J. Am. Chem. Soc.*, **94**, 5924 (1972).