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Thio Derivatives of 1,3-Diketones and Their Metal Complexes. Nickel(II), Palladium(II), and Platinum(II) Chelates of *O*-Ethyl Thioacetothioacetate

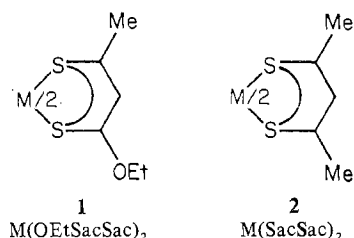
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The synthesis of low-spin d^8 square-coordinated nickel(II), palladium(II), and platinum(II) complexes of the sulfur chelating ligand *O*-ethyl thioacetothioacetate is described. Infrared, visible, ultraviolet, nuclear magnetic resonance, and mass spectra have been used to characterize the new complexes. $\text{Pt}(\text{OEtSacSac})_2$ can be crystallized into cis and trans isomers with respect to the peripheral OEt substituents. The corresponding geometric isomers of $\text{Ni}(\text{OEtSacSac})_2$ and $\text{Pd}(\text{OEtSacSac})_2$ display characteristic features in their nmr spectra but have not been separated. Comparison of the energies of the first d-d band in $\text{Ni}(\text{OEtSacSac})_2$ with $\text{Ni}(\text{II})$ complexes of other sulfur chelates indicate that the *O*-ethyl thioacetothioacetate anion occupies an intermediate position in a spectrochemical series of sulfur donors. Infrared and nmr data suggest that the substitution of a Me group in dithioacetylacetone by OEt concentrates electron density in the $\text{C}=\text{C}=\text{C}$ backbone of the chelate ring.

Introduction

As part of a continuing study on complexes of 1,3-dithio chelates,²⁻⁴ the spectroscopic characterization of the new complexes (1) of ethoxythioacetothioacetate with nickel(II),



palladium(II), and platinum(II) is presented. Previously, thorough studies have only been reported for 1,3-dithio chelates possessing aryl and alkyl substituents.⁵ The only palladium and platinum chelates studied so far are the dithioacetylacetonates $\text{M}(\text{SacSac})_2$ (2). With the complexes of *O*-ethyl thioacetothioacetate, abbreviated to $\text{M}(\text{OEtSacSac})_2$, the OEt substituent introduces asymmetry and the possibility of π -electron interaction with the six-membered chelate ring. Geometric isomers are to be anticipated, and although these have been sought for 1,3-dioxo chelates, none have been isolated or even detected.^{7,8} With 1,3-monothio ligands, geometric isomerization may occur at the MS_2O_2 core, although to date, only cis isomers have been characterized by X-ray crystallography.⁹⁻¹¹ The identification and characterization of cis and trans isomers of the present complexes of *O*-ethyl thioacetothioacetate are reported here together with their spectroscopic properties.

- (1) Research School of Chemistry, Australian National University.
- (2) (a) A. R. Hendrickson and R. L. Martin, *Aust. J. Chem.*, **25**, 257 (1972); (b) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Electrochem. Soc.*, **119**, 1325 (1972).
- (3) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Amer. Chem. Soc.*, **95**, 1449 (1973).
- (4) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).
- (5) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **24**, 2061 (1971).
- (6) G. A. Heath, Ph.D. Thesis, University of Melbourne, 1970.
- (7) J. J. Fortmann and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971).
- (8) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).
- (9) E. A. Shygam, L. M. Shkol'nikova, and S. E. Livingstone, *Zh. Strukt. Khim.*, **8**, 550 (1967).
- (10) J. Sieler, P. Thomas, E. Uhlemann, and E. Hohne, *Z. Anorg. Allgem. Chem.*, **380**, 160 (1971).
- (11) L. Kutschabsky and L. Beyer, *Z. Chem.*, **11**, 30 (1971).

Experimental Section

Analytical results are collected in Table I. Instrumental techniques are described in the previous paper.^{2a}

Bis(1-ethoxy-1-thiolobut-1-ene-3-thione)nickel(II) [$\text{Ni}(\text{OEtSacSac})_2$]. Method I. The crude sodium salt of $[\text{OEtSacSac}]^-$ was prepared as previously described^{2a} and dissolved cautiously in water. An aliquot of this solution was standardized against dilute hydrochloric acid by conductometric titration. The excess base (originating from unreacted NaH and NaOEt) was neutralized in the remaining solution. This solution of $[\text{OEtSacSac}]^-$ was used in the preparation of the complexes of the nickel triad.

The stoichiometric aliquot of $[\text{OEtSacSac}]^-$ was added with stirring to a solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in water. The deep brown precipitate, which was formed immediately, was filtered off, washed, dried, and recrystallized from a benzene-ethanol mixture as small brown crystals; yield of recrystallized product $\sim 70\%$.

Method II. OEtSacSacH (1.1 g) in MeOH (20 ml) was added with stirring to a warm solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.8 g) in MeOH (20 ml). After 0.5 hr the brown product was collected, washed, and dried. This crude material was recrystallized from a 1:9 mixture of CH_2Cl_2 and petroleum ether (bp 60–80°); yield $\sim 80\%$.

Method III. Sodium hydride (0.5 g of a 50% suspension in mineral oil) was slurried in dry DMSO (20 ml) and the mixture was cooled until a small proportion ($\sim 10\%$) of the DMSO solidified. *O*-Ethyl thioacetate (3.0 g) was added to the suspension dropwise with vigorous stirring. At the completion of reaction, judged by the cessation of hydrogen evolution (approximately 2 min), water (30 ml) was carefully added and the excess *O*-ethyl thioacetate was extracted into diethyl ether (three 20-ml portions). The aqueous solution was added to $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.5 g) in MeOH (40 ml) and the product was worked up as described in method I. The pure complex was separated by column chromatography on silica with a 30:70 mixture of CH_2Cl_2 and petroleum ether (bp 40–60°) and recrystallized from a mixture of acetone-petroleum ether; yield approximately 50%.

Bis(1-ethoxy-1-thiolobut-1-ene-3-thione)palladium(II) [$\text{Pd}(\text{OEtSacSac})_2$]. The stoichiometric quantity of $[\text{OEtSacSac}]^-$ solution (prepared as described above) was added to a solution of PdCl_2 in hot water and the mixture was stirred for 15 hr. The precipitate was filtered off, washed, and dried, and the complex was extracted into benzene. The volume of solvent was reduced, ethanol was added, and the crystals were collected. The pure complex was isolated from this mixture by chromatography on silica with petroleum ether (bp 60–80°) and was recrystallized from benzene-ethanol as fine orange-red crystals. This compound proved to be a mixture of cis and trans isomers.

Bis(1-ethoxy-1-thiolobut-1-ene-3-thione)platinum(II) [$\text{Pt}(\text{OEtSacSac})_2$]. This complex was prepared by the same method as $\text{Pd}(\text{OEtSacSac})_2$ in aqueous solution from K_2PtCl_6 . Precipitation commenced after 5 min at 20°. The product was isolated after 4 hr and recrystallized. Column chromatography on silica with an 80:20 petroleum ether-benzene mixture followed by recrystallization from benzene-ethanol afforded the pure product as deep red crystals. This product proved to be a mixture of cis and trans isomers.

Separation of Cis and Trans Isomers of $\text{Pt}(\text{OEtSacSac})_2$. The pure complex was dissolved in a 50% mixture of CH_2Cl_2 and EtOH at room temperature. The solution was covered and allowed to

Table I. Analytical and General Data

Compd	Color	Analytical data					
		Calcd	% C	% H	% S	% metal wt ^b	
Ni(OEtSacSac) ₂ ^a	Brown	Calcd	37.8	4.8	33.6	15.4	381
		Found-I	37.3	4.4	34.3	15.4	361
		Found-II	37.8	4.8	34.1	15.7	
		Found-III	37.6	4.6	33.8	15.9	
Pd(OEtSacSac) ₂ ^a	Orange-red	Calcd	33.6	4.2	29.9	24.8	429
		Found	33.9	4.1	29.1	25.2	431
Pt(OEtSacSac) ₂ ^a	Red	Calcd	27.9	3.5	24.8	37.7	518
		Found	27.8	3.5	22.2	37.8	548
Ni(OEtacSac) ₂		Calcd	41.3	5.2	18.4	16.8	
		Found	41.2	5.3	18.3	16.7	
Ni(OMeacSac) ₂		Calcd	37.4	4.4	20.0	18.3	
		Found	37.4	4.4	20.0	17.9	

^a Mixture of cis and trans isomers. ^b By vapor pressure osmometry in benzene.

evaporate slowly. Two distinct crystal types formed and were separated manually. This was most readily achieved by placing the dry crystals on a sheet of smooth paper held at an angle of approximately 30° to the horizontal and gently tapping it. The long thin plates adhered to the surface while the chunky crystals tumbled down the incline.

Bis(1-ethoxy-1-oxobut-1-ene-3-thione)nickel(II) [Ni(OEtacSac)₂]. This compound was prepared from *O*-ethyl thioacetate (OEtacSacH) and nickel acetate as described in the literature.¹²

Bis(1-methoxy-1-oxobut-1-ene-3-thione)nickel(II) [Ni(OMeacSac)₂]. This compound was prepared from *O*-methyl thioacetate and nickel(II).¹²

Results and Discussion

The new, crystalline compounds are readily prepared from [OEtSacSac]⁻ and the metal ions. The complexes are appreciably lighter in color than the corresponding dithioacetylacetonato compounds, varying from brown to orange-red to red on progressing from nickel to palladium to platinum. The corresponding [SacSac]⁻ compounds are red-violet, red, and purple.¹³ The paler colors of these compounds raise the possibility of readily distinguishing the d-d transitions from the charge-transfer bands of these complexes.

The compounds possess a faint although not unpleasant odor and are stable to air and moisture. They are quite soluble in most organic solvents although insoluble in alcohols and water. The diamagnetic complexes are monomeric in solution (Table I) and are assumed to be square-coordinated, analogous to the structure of Ni(SacSac)₂¹⁴ and other diamagnetic four-coordinate thio chelates of nickel(II).¹⁵

Single-crystal X-ray studies¹⁶ on the two crystalline forms of Pt(OEtSacSac)₂ definitely establish that the complex exists as cis and trans isomers.

The geometric isomers of Pd(OEtSacSac)₂ and Pt(OEtSacSac)₂ cannot be separated by the usual techniques (*e.g.*, fractional crystallization or chromatography). However, the isomers of Pt(OEtSacSac)₂ can be induced to crystallize in substantially different crystalline forms. Careful crystallization of Pt(OEtSacSac)₂ affords a mixture of small chunky crystals (trans) and large flat plates (cis) which have been satisfactorily separated by hand. The crystals of Pd(OEtSacSac)₂ are much smaller and separation of these isomers has not been accomplished.

The compounds are quite volatile and mass spectra are

(12) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

(13) R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).

(14) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

(15) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(16) B. F. Hoskins and D. McElholm, unpublished results.

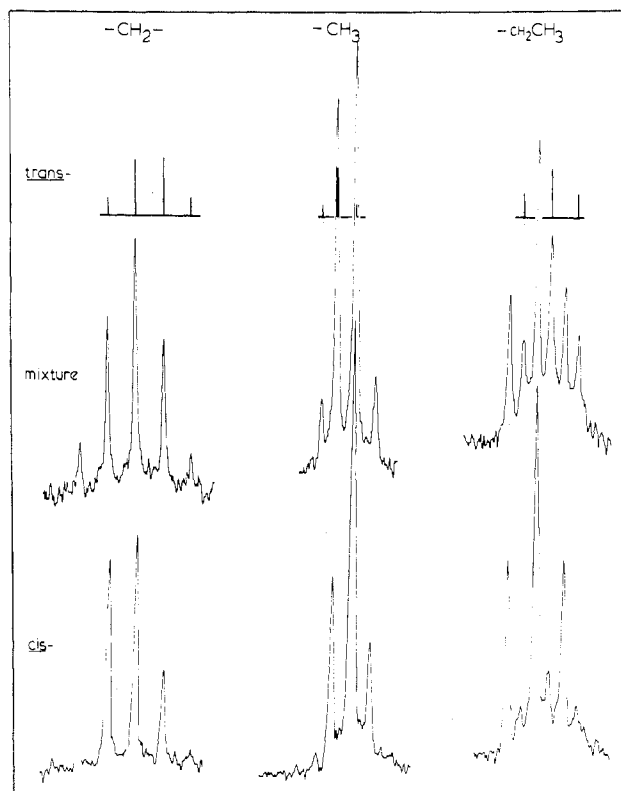


Figure 1. Nmr spectra of geometric isomers of Pt(OEtSacSac)₂. The spectrum of the trans isomer is only shown schematically.

readily obtained. The parent ions [M(OEtSacSac)₂]⁺ and the [M(OEtSacSac)]⁺ fragments are obtained for the nickel triad of complexes although peaks at *m/e* 133 and 161 constitute the most abundant ions. As discussed in an earlier paper^{2a} the ions at *m/e* 133 and 161 are believed to be the resonance stabilized 3-methyl-5-hydroxy- and 3-methyl-5-ethoxy-1,2-dithiolium cations, respectively. A broad metastable peak at *m/e* 109.9, present in the spectra of the three complexes, is compatible with the expulsion of C₂H₄ (or less likely CO) from the *m/e* 161 ion giving rise to the *m/e* 133 ion.

(i) **Nmr Spectra.** The relatively high solubility of the present diamagnetic complexes in CDCl₃ and benzene-*d*₆ has enabled excellent high-resolution nmr spectra to be obtained.

The spectrum of Ni(OEtSacSac)₂ is well resolved and readily assigned on the basis of integration and the characteristic internal coupling of the ethyl group. The spectral features are similar to those of Zn(OEtSacSac)₂.^{2a} In CDCl₃ the two crystalline forms of Pt(OEtSacSac)₂ possess identical spectra except for a slight separation of the -CH₂- resonances (1.3 Hz at 27°). In hexadeuteriobenzene all peaks of the two isomers have slightly different chemical shifts except the methine resonances (Figure 1, Table II). Interestingly, the relative shift values of the two isomers may be rationalized in terms of solvent-accentuated dipole effects.

As the two isomers of Pt(OEtSacSac)₂ incorporate the same metal ion and ligands and differ only at the periphery of the molecule, it seems reasonable to assume that the small differences in chemical shift values for these groups in the cis and trans isomers should reflect the difference in dipole moments of the isomers.

If the molecular dipole moment is directed across the molecule from OEt(+) to Me(-), the deduced, relative shifts of the cis and trans isomers would agree with those experi-

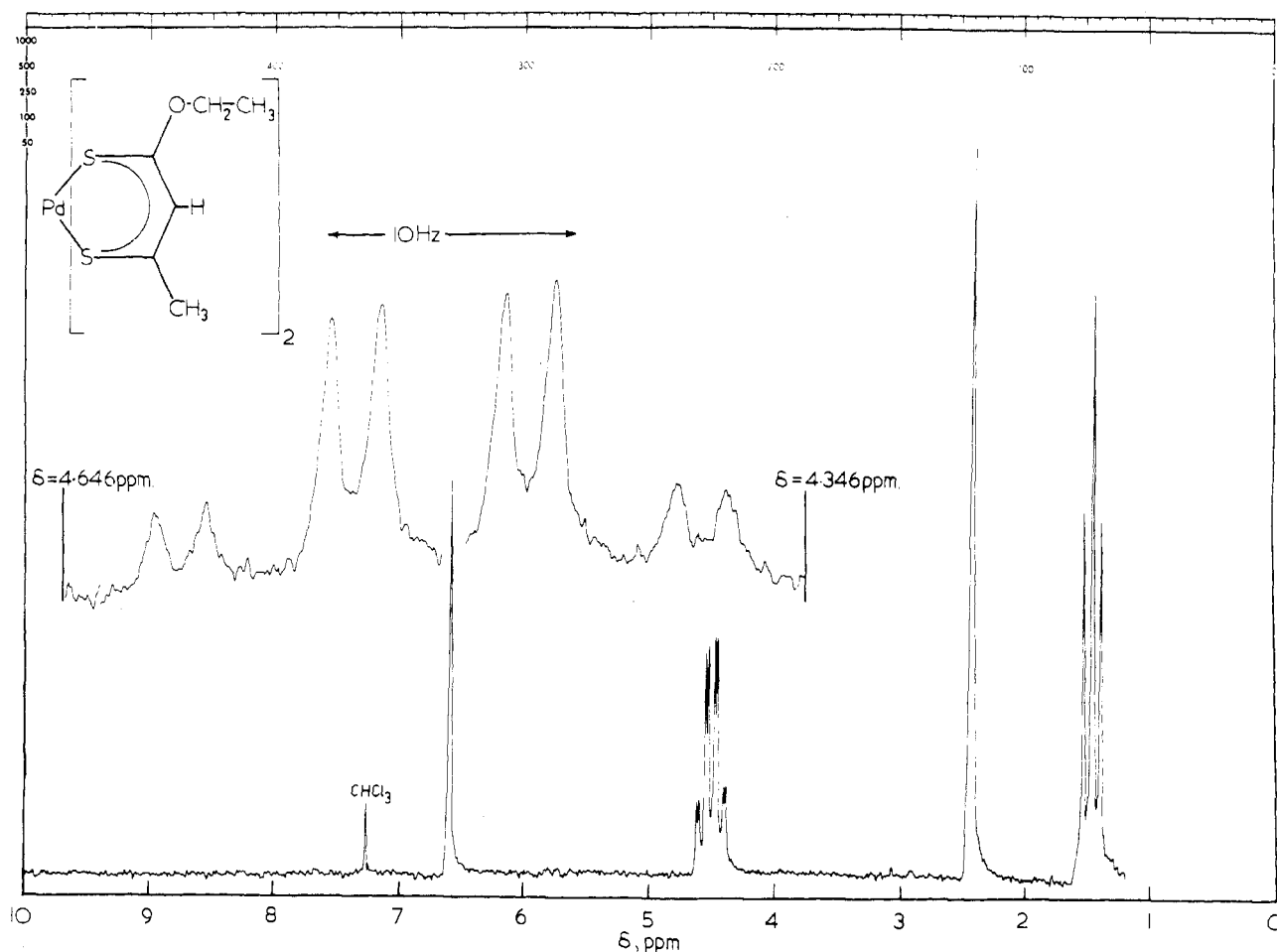


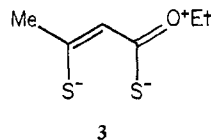
Figure 2. Nmr spectrum of a 50% mixture of *cis*- and *trans*-Pd(OEtSacSac)₂ in CDCl₃.

Table II. Nmr Data in Benzene-*d*₆ (All *J*_{CH₃-CH₂} = 7.0 Hz)

Compd ^a	δ , ppm (with ref to internal TMS ^b)			
	CH ₃ —	CH ₂	H	CH ₃
Ni(OEtSacSac) ₂	0.92	4.04	6.46	2.00
<i>cis</i> -Pd(OEtSacSac) ₂	0.93	4.05	6.46	2.06
<i>trans</i> -Pd(OEtSacSac) ₂	0.91	3.99	6.46	2.11
<i>cis</i> -Pt(OEtSacSac) ₂ (long crystals)	0.94	3.95	6.43	1.79
<i>trans</i> -Pt(OEtSacSac) ₂ (short crystals)	0.90	3.89	6.43	1.86

^a Tentative *cis* and *trans* assignments discussed in text. ^b TMS = tetramethylsilane at δ 0.00 ppm.

mentally observed. This rationalization implies a significant contribution of the canonical form



in these complexes. Shortening of C—O and one C—C bond as observed in the crystal structure of the zinc complex of this ligand¹⁷ supports this interpretation.

Although the *cis* and *trans* isomers of Pd(OEtSacSac)₂ have not been separated, nmr confirms their existence. Thus the nmr spectra of Pd(OEtSacSac)₂ isomers in CDCl₃ solution exhibit a small difference in chemical shifts for the

—CH₂— groups only (2.1 Hz at 27°), Figure 2, although these isomers display identical spectra in 1,2-dichloroethane. In benzene-*d*₆ the chemical shifts of the protons of *cis*- and *trans*-Pd(OEtSacSac)₂ are separated sufficiently to extract the chemical shift parameters for each isomer in this solvent (Table II). Assignment of the spectrum is facilitated by the 40:60 mixture of isomers in the purified sample as the complete set of peaks for each isomer is readily and unambiguously discerned from the relative intensities of each set. Assignment of isomers has been made by analogy with those of Pt(OEtSacSac)₂.

The difference in chemical shift values of the methylene resonances of Pd(OEtSacSac)₂ in CDCl₃ (50% mixture of isomers) shows a slight convergence, 2.1 → 2.0 Hz, on increasing temperature (30–50°).

In CHBr₃, this investigation has been extended to 130°, at which the methylene resonances of the two isomers merge (Figure 3). Figure 4 traces the temperature dependence of this process. Although this evidence suggests rapid isomeric interchange, such an interpretation must be treated cautiously. The merging of nmr signals, for entities related by a rapid-exchange process, is expected to pass through a broad coalesced signal.¹⁸ As Figure 3 shows, the present relatively sharp signals merge by a change in chemical shift difference. Whether this process reflects a rapid isomer interchange or simply a fortuitously different temperature dependence of the chemical shifts for the isomers is not apparent in view of

(17) R. Beckett and B. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, **8**, 679 (1972).

(18) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965.

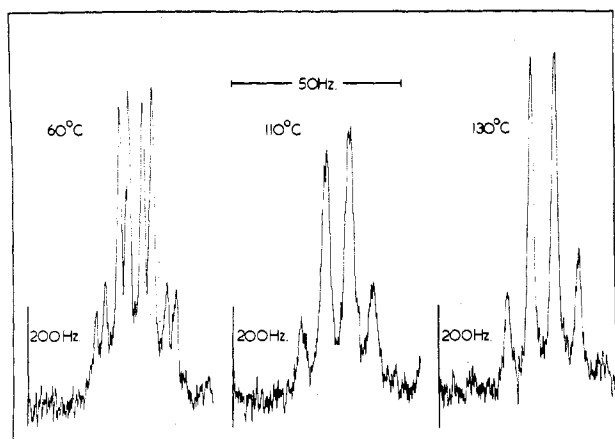


Figure 3. Temperature dependence of methylene signals ($\text{Pd}(\text{OEtSacSac})_2$ in CHBr_3).

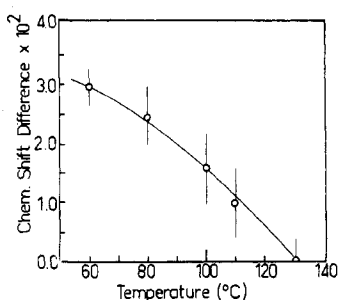


Figure 4. Temperature dependence of separation of methylene signals for isomers of $\text{Pd}(\text{OEtSacSac})_2$.

the very small (<0.03 ppm) chemical shift differences between the methylene resonances of the isomers. However, the results do reveal that the cis-trans isomer equilibrium position is not shifted over this large temperature range. With regard to the interconvertibility of the isomers it has been noted that slow recrystallization of a pure sample of one isomer of $\text{Pt}(\text{OEtSacSac})_2$ affords crystals of both isomeric forms.

$\text{Ni}(\text{OEtSacSac})_2$ exhibits only one set of sharp resonances in either CDCl_3 or benzene- d_6 at room temperature. Spectra which have been measured at instrument sensitivities capable of resolving methyl-methine proton spin coupling (0.005 ppm at 100 MHz) exhibit no anomalies attributable to isomers. However, on cooling a CDCl_3 solution of $\text{Ni}(\text{OEtSacSac})_2$ to -15° , the methylene quartet exhibits broadening and at -40° two quartets of equal intensity are apparent, separated by 2.2 Hz. This spectrum is exactly analogous to the room-temperature spectra of $\text{Pd}(\text{OEtSacSac})_2$ and $\text{Pt}(\text{OEtSacSac})_2$ in CDCl_3 , indicating the three complexes examined comprise cis and trans isomers.

The large differences in the chemical shift data of the complexes in CDCl_3 and benzene- d_6 suggest a specific interaction is operative between benzene and the complexes. The literature abounds with species (usually organic) which display similar behavior.^{19,20}

The utility of benzene- d_6 for shifting nmr absorptions that appear equivalent in other solvents has been checked with the closely related compound $\text{Ni}(\text{SacSac})(\text{Sacac})$ (4) which

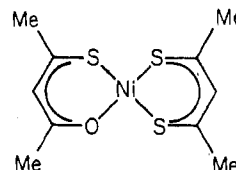
Table III. Methyl Nmr Absorptions in CDCl_3 and Benzene- d_6

Solvent	Compd with δ , ppm (internal TMS)				
	$\text{Ni}(\text{SacSac})_2$ S	$\text{Ni}(\text{SacSac})(\text{Sacac})$		$\text{Ni}(\text{Sacac})_2$	
		S	S	O	S
CDCl_3 ²¹	2.31	2.25 (3) ^a	2.04 (1)	2.17 (1)	2.10 (1)
Benzene- d_6	1.88	1.92 (1) ^b 1.80 (2) ^c	1.49 (1)		

^a Numbers in parentheses are the estimated relative peak areas.

^b Assigned to the methyl group adjacent to sulfur in $[\text{Sacac}]^-$.

^c Assigned to the methyl groups in $[\text{Sacac}]^-$.



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displays only two sharp methyl absorptions in CDCl_3 (δ 2.04 and 2.35 ppm) which have been assigned unambiguously on the basis of integrated peak areas to methyl groups adjacent to oxygen and sulfur groups, respectively.²¹

However, in benzene the spectrum exhibits three sharp resonances (Table III). The resonance at 1.80 ppm is assigned to the methyl groups on the $[\text{Sacac}]^-$ ligand on the basis of the number of protons. In CDCl_3 the downfield methyl resonance of the $[\text{Sacac}]^-$ ligand in $\text{Ni}(\text{Sacac})_2$ and $\text{Ni}(\text{SacSac})(\text{Sacac})$ has been unambiguously assigned in both compounds to the methyl group adjacent to the sulfur atom.²¹ These assignments have been based on intensity data and contact-shifted nmr spectra.²² It is felt that this ordering is unlikely to be altered in the present instance and the resonances of the $[\text{Sacac}]^-$ ligand are assigned accordingly (Table III).

In the absence of rapid exchange, the two methyl groups on the $[\text{Sacac}]^-$ ligand in $\text{Ni}(\text{SacSac})(\text{Sacac})$ should not be exactly equivalent. A further very useful method for spreading inequivalent resonances, although of limited scope, is the induction of paramagnetism into the complex to give a contact-shifted nmr spectrum. $\text{Ni}(\text{Sacac})_2$ is sensitive to axial perturbations and the contact-shifted spectrum of $\text{Ni}(\text{Sacac})_2(\text{py})_2$ has been thoroughly studied by La Mar.²² Unfortunately, stepwise addition of pyridine (up to approximately 40% solution) shows $\text{Ni}(\text{SacSac})(\text{Sacac})$ in benzene- d_6 undergoes no significant axial interaction. The three methyl resonances simply move downfield ~ 0.2 ppm. This shift is well within the range expected for a simple solvent change. Under the same experimental conditions of addition of pyridine to $\text{Ni}(\text{Sacac})_2$ in benzene- d_6 the methyl resonances also shift ~ 0.2 ppm downfield.

Although the differentiating property of benzene is extremely useful in the instances described above, it has been noted that this solvent probably introduces spurious trends in more general comparisons.²³ Hence the general discussion of the nickel, palladium, and platinum complexes of $[\text{OEtSacSac}]^-$ and related ligands is restricted to the results obtained in the less "interacting" solvent CDCl_3 (Table IV).

A meaningful comparison of the effect on the proton nmr absorptions by successive replacement of the oxygen atoms in $\text{Ni}(\text{OEtacac})_2$ is not possible as $\text{Ni}(\text{OEtacac})_2$ is para-

(19) J. Ronayne and D. H. Williams, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 83 (1969).

(20) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967).

(21) C. G. Barraclough, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).

(22) G. N. La Mar, *Inorg. Chem.*, **8**, 581 (1969).

(23) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, 1749 (1966).

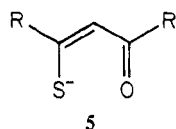
Table IV. Nmr Spectral Data

Compd	Chem shift, ^a ppm				$J_{\text{CH}_3-\text{CH}_2}$, Hz	$J_{\text{CH}_3-\text{H}}$, Hz	Solvent
	CH ₃	CH ₂	H	CH ₃			
Ni(OEtSacSac) ₂	1.38	4.46	6.59	2.31	7.1	~0.4	CDCl ₃
Pd(OEtSacSac) ₂	1.43	{4.48 4.50	6.59	2.40	7.1		CDCl ₃
Pt(OEtSacSac) ₂	1.44	{4.40 4.42	6.58	2.18	7.0	<i>b</i>	CDCl ₃
Ni(OEtacSac) ₂	1.25	4.08	5.76	2.10	7.4	~0.7	CDCl ₃
Ni(OMeacSac) ₂	3.68	(OCH ₃)	5.78	2.11			CDCl ₃
Ni(SacSac) ₂ ^c			7.06	2.31			CDCl ₃
Ni(Sacac) ₂ ^c			6.41	{2.10 2.17			CDCl ₃
OEtSacSacH ^d	1.40	4.46	6.42	2.21	7.0	1.0	CCl ₄
OEtSacSacH ^d	1.36	4.43	6.44	2.17	7.0		CDCl ₃
OEtacSacH ^e	1.27	4.13	5.75	2.13		1.2	CCl ₄
OEtacacH	1.25	4.14	4.97	1.94	7		CDCl ₃
CH ₃ C(S)OEt	1.36	4.44		2.50	7.0		CDCl ₃

^a Internal reference tetramethylsilane, at δ 0.00 ppm. ^b For ¹⁹⁵Pt-H coupling, see Table V. ^c Reference 21. ^d Reference 2a. ^e J. Duss and S.-O. Lawesson, *Ark. Kemi*, **29**, 127 (1968).

magnetic, polymeric, and insoluble in the usual solvents.²⁴ The complex exhibits a slight solubility in DMF but unfortunately dissolves as a paramagnetic disolvate.

Interestingly the coupling constant $J_{\text{CH}_3-\text{H}}$ is significantly larger for the monothio complex ($J = 0.7$ Hz) than the dithio complex ($J = 0.4$ Hz) of nickel(II) which may reflect the tendency of the monothio ligand to adopt the thio-enol form in its complexes, with the coupling between the methyl and methine protons being enhanced by the comparative localization of the double bond between these groups. This



phenomenon has been observed for all the 1,3-monothio complexes studied by X-ray crystallography, assuming bond length is a measure of bond order.^{9-11,25} The comparable coupling constant for OEtSacSacH ($J = 1.0$ Hz), being much larger than that of the complexed ligand, is entirely consistent with the localization of the C=C bond in the free ligand.^{2a}

The methyl groups on Ni(OEtSacSac)₂ and Ni(SacSac)₂ exhibit very similar chemical shift values although the larger upfield shift of the ring (methine) proton in Ni(OEtSacSac)₂ reflects the relative effects of the OEt and Me groups on the electron density in this region with an apparent enriched electron density in the backbone of the M(OEtSacSac)₂ complexes. The ir absorption energies of the C=C stretching mode (*vide infra*) support this conclusion. This enhanced electron density is suggested to originate from partial delocalization of π_p electrons of the oxygen onto the chelate ring as noted in the discussion of the geometric isomers of Pt(OEtSacSac)₂.

¹⁹⁵Pt-H coupling constants for Pt(OEtSacSac)₂ and related platinum compounds are collected in Table V. The Pt-H coupling constants are the same for both isomers of Pt(OEtSacSac)₂.

(ii) **Infrared Spectra.** The new complexes exhibit closely similar ir spectra and the relative intensity trends are similar to those of Zn(OEtSacSac)₂.^{2a} As expected, the ir spectrum of M(OEtSacSac)₂ is more complex than that of M(SacSac)₂. However, as the basic six-membered chelate structure is a

Table V. Pt-H Coupling Constants

Compd	$J_{\text{Pt}-\text{CH}}$, Hz	$J_{\text{Pt}-\text{CH}_3}$, Hz
Pt(acac) ₂	11 ^a	5 ^a
	10.6 ^b	4.8 ^b
Pt(SacSac) ₂	<i>d</i>	9 ^c
Pt(OEtSacSac) ₂	6.2	8.6

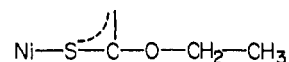
^a J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965). ^b P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, **6**, 781 (1967). ^c Reference 6. ^d Not resolved due to limited solubility.

common feature, the normal-coordinate analysis of square-planar dithioacetone complexes²¹ has been drawn on to assign the common vibrations.

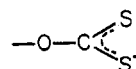
Table VI indicates the common assignment of Ni(SacSac)₂ and Ni(OEtSacSac)₂, the correlation holding for both absorption energies and relative intensities.

The $\nu(\text{C}=\text{C})$ band of Ni(OEtSacSac)₂ is 19 cm⁻¹ higher in energy than the corresponding band in Ni(SacSac)₂ consistent with an enhanced electron density in the C=C backbone of Ni(OEtSacSac)₂. Assignment of both the 820- and 824-cm⁻¹ peaks to the C-H out-of-plane bending mode is based on the observation that the ~830-cm⁻¹ band in many complexes of [SacSac]⁻ is similarly split by a few wave numbers.^{5,6,26}

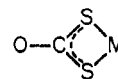
As the



fragment of Ni(OEtSacSac)₂ is structurally similar to the same unit in bis(ethyl xanthato)nickel(II), the ir assignments of Ni(EtXan)₂²⁷ and [EtXan]⁻²⁸ have been used for the present assignment. Although the ethyl xanthate anion has significantly different absorption energies for bands associated with the



unit as compared with the



(26) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).

(27) U. Agarwala, Lakshmi, and P. B. Rao, *Inorg. Chim. Acta*, **2**, 337 (1968).

(28) A. T. Pilipenko and N. V. Mel'nikova, *Russ. J. Inorg. Chem.*, **15**, 608 (1970).

(24) R. W. Hay and G. E. R. Hook, *Aust. J. Chem.*, **17**, 601 (1964).

(25) S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, **91**, 2504 (1969).

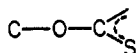
Table VI. Ir Absorptions of Ni(OEtSacSac)₂ and Related Compounds

Assignment ^a	Ni-(EtXan) ₂ ^b	Ni-(OEtSacSac) ₂	Ni-(SacSac) ₂	Assignment ^c
$\nu(\text{C-H})$	2980	2980		
$\nu(\text{C-H}) (\text{CH}_3)$	2950	2953		
$\nu(\text{C-H})$	2937	2938		
$\nu(\text{C-H}) (\text{CH}_2)$	2890	2880		
$\nu(\text{C-H}) (\text{CH}_3)$	2858			
CH ₃ mode	1463	1510	1491	$\nu(\text{C} \cdots \text{C}) + \delta(\text{C-H})$
		1469		
		1440	1430	CH ₃ deg def
$\delta(\text{C-H})$	1440	1392		
CH ₃ def	1389	1370	1351	CH ₃ sym def
<i>d</i>	1368	1344	1344	$\nu(\text{C-C})$
		1324	1312	$\delta(\text{C-H})$
		1290	1290	$\delta(\text{C-H})$ } in plane
		1272		
$\nu(\text{C-O})$	1268	1203		
		1150	1157	$\nu(\text{C-CH}_3) ?$
		1111		
$\nu(\text{C-O})$	1115	1092		
$\delta(\text{C-H})$	1059	1038	1020	} CH ₃ rock modes
		1018	1010	
		1006		
$\nu(\text{CH}_2-\text{CH}_3)$	857	901		
		824	830	$\delta(\text{C-H})$ out of plane
		820		
CH ₂ scissor	810	746		
		692	748	$\nu(\text{C} \cdots \text{S}) + \nu(\text{C-CH}_3)$
		639	703	$\nu(\text{C} \cdots \text{S})$
		502	555	$\nu(\text{C-CH}_3) + \text{ring def}$
Varying contribution of $\nu(\text{M-S})$ }	437	411		
	383	364	365	$\nu(\text{Ni-S})$
	351			

^a U. Agarwala, Lakshmi, and P. B. Rao, *Inorg. Chim. Acta*, 2, 337 (1968); A. T. Pilipenko and N. V. Mel'nikova, *Russ. J. Inorg. Chem.*, 15, 608 (1970). ^b Only relevant peaks listed (see text). ^c Reference 21. ^d Complex mode; involves $\nu(\text{C} \cdots \text{C})$ and other vibrations.

unit, C-H modes are relatively unaffected by coordination. Comparison of the peaks in the spectrum of Ni(OEtSacSac)₂ with the relevant peaks in the spectrum of Ni(EtXan)₂ reveals an excellent correlation of peaks attributable to C-H modes associated with the OEt unit (Table VI).

Absorptions due to the



unit in Ni(OEtSacSac)₂ are assigned with less certainty. The vibrational modes for this moiety are substantially coupled and direct comparisons between the two complexes are no longer strictly valid. However, the important assignment of the 1203-cm⁻¹ peak in Ni(OEtSacSac)₂ to the C-O stretch is reasonably conclusive, based on (i) the similar position of the band in both complexes, (ii) the dominating intensity of the band in both cases, and (iii) the absence of a similar band in Ni(SacSac)₂.

The $\nu(\text{C} \cdots \text{S})$ band (57%²⁹) in Ni(SacSac)₂ at 703 cm⁻¹ is heavily coupled with other modes, chiefly the C-CH₃ stretch. The $\nu(\text{C} \cdots \text{S})$ mode is believed to be a major contributor to the 639 cm⁻¹ absorption in Ni(OEtSacSac)₂. Ni(EtXan)₂ exhibits three peaks, possessing substantial contributions from M-S stretching modes (Table VI). Although Ni(SacSac)₂ exhibits only a single $\nu(\text{M-S})$ band (360 cm⁻¹, 57%) a band at 449 cm⁻¹ [$\delta(\text{C-CH}_3)$ (55%) + $\nu(\text{M-S})$ (31%)] has been predicted for Co(SacSac)₂ from the normal-coordinate analysis.²¹ The band has not been observed. These points suggest that the two bands at 411 and 364 cm⁻¹ in Ni(OEtSacSac)₂ have considerable $\nu(\text{M-S})$ character.

The spectra of the palladium(II) and platinum(II) com-

Table VII. Ir Spectra of M(OEtSacSac)₂ Complexes (cm⁻¹)

Ni-(OEt-SacSac) ₂	Pd-(OEt-SacSac) ₂	Pt-(OEt-SacSac) ₂	Assignment
1510	{1509 1500}	{1508 1495}	$\nu(\text{C} \cdots \text{C}) + \delta(\text{C-H})$
1469	1468	1461	} C-H modes
1440	1449	1447	
	1439	1432	
1392	1390	1390	$\delta(\text{C-H})$
1370	1364	1365	CH ₃ sym def
1344	1341	1341	$\nu(\text{C-C})$
1324	1324	1311	} $\delta(\text{C-H})$ in plane
1290	1295	1295	
1272	1278	1261	
1203	{1204 1195}	1193	$\nu(\text{C-O})$
1150	1149	1150	} $\nu(\text{C-CH}_3) ?$
1111	1111	1108	
1092	1089	1090	$\nu(\text{C-O})$
1038	1034	1035	$\delta(\text{C-H})$
1018	1016	1013	} CH ₃ rock modes
1006	1002	1000	
901	896	891	$\nu(\text{CH}_3-\text{CH}_2)$
		845	
		839	} $\delta(\text{C-H})$ out of plane
824	822	822	
820	818	815	
746	745	746	CH ₂ scissor
692	691	691	$\nu(\text{C} \cdots \text{S}) + \nu(\text{C-CH}_3)$
639	639	637	$\nu(\text{C} \cdots \text{S})$
502	508	507	$\nu(\text{C-CH}_3) + \text{ring def}$
411	405	402	$\nu(\text{M-S}) ?$
364	379	367	$\nu(\text{M-S})$

plexes of [OEtSacSac]⁻ are assigned as for the nickel(II) complexes (Table VII).

(iii) **Electronic Spectra.** The electronic spectra in the region 10,000-45,000 cm⁻¹ of Ni(OEtSacSac)₂, Pd(OEt-

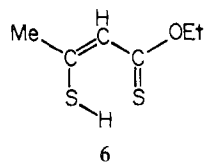
(29) The percentage contributions quoted for the [SacSac]⁻ compounds have been evaluated for Co(SacSac)₂.²¹

SacSac)₂, and *cis*- and *trans*-Pt(OEtSacSac)₂ are compared with that of the free ligand OEtSacSacH in Table VIII. The metal complexes are characterized by a progression of intense bands, a number of which are broad and not fully resolved.

A comparison between the principal spectral features of the square-planar compounds Ni(SacSac)₂ and Ni(OEtSacSac)₂ and the tetrahedral complex Zn(OEtSacSac)₂ is also given in Table VIII. The spectra of Ni(SacSac)₂ and Ni(OEtSacSac)₂ show an almost 1:1 correlation of peak positions and intensity trends confirming that the perturbation introduced by substituting OEt for one Me group in each ligand is small but significant. Thus the band at 18,120 cm⁻¹ has moved to higher energy (*ca.* 2500 cm⁻¹) leaving the lowest energy d-d band completely resolved and revealing the next d-d band as a well-defined shoulder. The tentative assignments in Table VIII (assuming D_{2h} symmetry) refer to an axis system with *z* perpendicular to the plane of the molecule and *x* and *y* in the plane, directed between the sulfur donor atoms.

The energy of the first d-d transition of Ni(OEtSacSac)₂ remains unaltered in the presence of strongly coordinating solvents, *e.g.*, pyridine, suggesting that axial perturbations are quite small for the complex, and substantiates the assignment of this band to d orbitals in the *x-y* plane of the molecule, *i.e.*, d_{x²-y²} → d_{xy}. The corresponding absorption in other square-coordinated sulfur chelates of divalent nickel, assuming the band originates from the same transition in all examples, places the ligands in the following spectrochemical order: [S₂CC(CN)COOEt]²⁻³⁰ (16,700 cm⁻¹) > [CS₃]²⁻³⁰ (16,400 cm⁻¹) > [S₂CC(CN)C(O)NH₂]²⁻³⁰ (16,000 cm⁻¹) ≈ [S₂CNCN]²⁻³⁰ (15,870 cm⁻¹) ≈ diethyldithiocarbamate³¹ (15,800 cm⁻¹) ≈ [S₂CC(CN)₂]²⁻³⁰ (15,700 cm⁻¹) ≈ ethyl xanthate³¹ (15,500 cm⁻¹) > [SacSac]⁻ (14,800 cm⁻¹) ≈ [OEtSacSac]⁻ (14,700 cm⁻¹) ≈ diethyl dithiophosphate³¹ (14,500 cm⁻¹) > dithiophosphate³² (13,700 cm⁻¹) ≈ dithiocacodylate³³ (13,700 cm⁻¹) > maleonitriledithiolate dianion³⁴ (11,690 cm⁻¹). This order is also observed with the corresponding Cr(chelate)₃ compounds.³³

The close similarity between the absorption maxima at ~30,000 and ~36,000 cm⁻¹ for the d⁸ (Ni) and d¹⁰ (Zn) complexes suggests that this region of the spectrum is dominated by transitions characteristic of the coordinated ligand alone. This correspondence appears to extend in part to the protonated form of the ligand where the double bonds are believed to be localized as in 6.^{2a} The assignment of these



bands to L → L* transitions and the assignment of the d-d bands is basically in agreement with the calculations attempted by Siimann and Fresco, who employed semiempirical Wolfsberg-Helmholz MO methods.³⁵

However, Siimann and Fresco have also employed their MO scheme to assign the electronic spectrum of Co(SacSac)₂.

(30) J. P. Fackler, Jr., and D. Coucouvanis, *J. Amer. Chem. Soc.*, **88**, 3913 (1966).

(31) C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(32) W. Kuchen and A. Judat, *Chem. Ber.*, **100**, 991 (1967).

(33) A. T. Casey, D. J. Mackey, and R. L. Martin, *Aust. J. Chem.*, **24**, 1587 (1971).

(34) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 4594 (1964).

(35) O. Siimann and J. Fresco, *J. Amer. Chem. Soc.*, **92**, 2652 (1970).

Table VIII. Electronic Spectra of OEtSacSacH and Its Ni(II), Pd(II), and Pt(II) Complexes (Cyclohexane)

Zn(OEtSacSac) ₂ ^a	Ni(SacSac) ₂ ^b		Ni(OEtSacSac) ₂		Pd(OEtSacSac) ₂		Pt(OEtSacSac) ₂		OEtSacSacH ^a		Tentative assignments for the complexes
	ν , cm ⁻¹	ϵ	ν , cm ⁻¹	ϵ	ν , cm ⁻¹	ϵ	Short crystals ν , cm ⁻¹	Long crystals ν , cm ⁻¹	ν , cm ⁻¹	ϵ	
24,000	14,890	330	14,700	101	19,100?	900	19,700	19,700	24,100	290	$x^2 - y^2 \rightarrow xy$
25,600	18,120	2,820	17,500	385	21,700	5,790	28,500	28,300	29,600 sh		$xz \rightarrow xy$
31,000	25,510	4,160	20,600	4,560	22,800	8,500	30,500	30,400	30,400	10,900	L → L*
	29,670	21,500	25,000	4,830	29,400	11,850	36,400	36,600	35,500 sh	8,000	L → L*
36,100	35,460	38,900	29,300	25,360	34,100	31,600	41,300	41,300	36,900		
	36,500	45,700	36,600	79,060	39,700	92,300	43,500	42,700	37,200		
	41,150	17,000	42,000	30,720	40,500	35,400	43,500	33,400			
					41,500	46,000					

^a Reference 2a. ^b Reference 35.

Their 2A_g ground state, based on the configuration $[(yz)^2 - (z^2)^2(xz)^2(x^2 - y^2)^1]$, is at variance with the results of paramagnetic anisotropy and esr measurements which favor the ground configuration $[(yz)^2(xz)^2(x^2 - y^2)^2(z^2)^1]$.³⁶ The large magnetic anisotropy observed in the CoS_4 plane then originates from the proximity in energy of the z^2 and xz levels relative to the more stable yz level. For the above reasons the detailed assignments of Siimann and Fresco, based on semiempirical MO calculations, must be regarded with caution.

The principal absorption bands of the palladium(II) and platinum(II) complexes are also listed in Table VIII. The bands appear to fall in similar energy regions to those of $Ni(OEtSacSac)_2$. The spectra of *cis*- and *trans*- $Pt(OEtSacSac)_2$ differ little (see Figure 5) providing direct evidence that, although the effect of differing symmetry is readily detectable, the presence of one OEt group per ligand does not greatly modify the spectra. For the palladium and platinum complexes, only $Pd(OEtSacSac)_2$ exhibits a band (ν 19,100 cm^{-1}) with a molar absorbance (ϵ 900) sufficiently low to be assigned as a ligand field transition. $Pt(OEtSacSac)_2$ exhibits a strong absorption (ϵ 5300) at 19,700 cm^{-1} which is suffi-

(36) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).

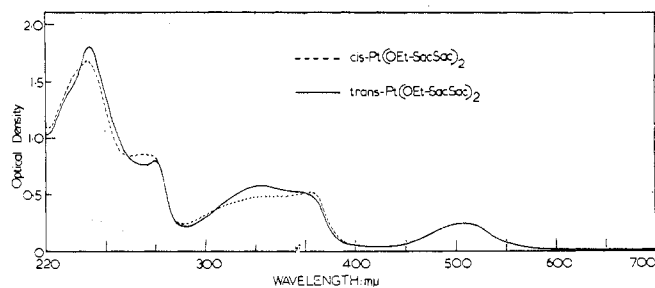


Figure 5. Electronic spectra of *cis*- and *trans*- $Pt(OEtSacSac)_2$.

ciently intense to mask weaker bands. Although the tabulated spectrum of $Pd(OEtSacSac)_2$ has been obtained from a mixture of *cis* and *trans* isomers, this is not expected to introduce spurious results. This conclusion is based on the close similarity of the spectra of *cis*- and *trans*- $Pt(OEtSacSac)_2$ (Figure 5).

Acknowledgments. A. R. H. gratefully acknowledges the CSIRO for a postgraduate studentship.

Registry No. $Ni(OEtSacSac)_2$, 41523-92-6; *cis*- $Pd(OEtSacSac)_2$, 41523-93-7; *trans*- $Pd(OEtSacSac)_2$, 41523-94-8; *cis*- $Pt(OEtSacSac)_2$, 41523-95-9; *trans*- $Pt(OEtSacSac)_2$, 41523-96-0; $Ni(SacSac)_2$, 10170-79-3; $Ni(SacSac)(Sacac)$, 41523-98-2; $Ni(OEtacSac)_2$, 14239-81-7; $Ni(OMeacSac)_2$, 14301-90-7.

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Synthetic Approaches to 14-, 15-, and 16-Membered Tetraaza Macrocycles and Their Metal Complexes

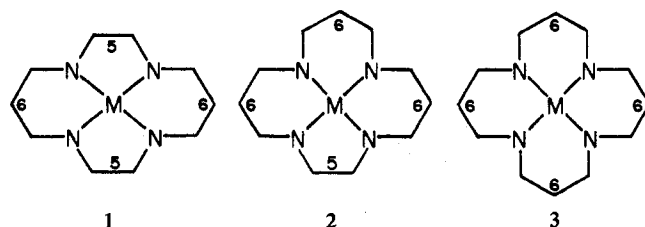
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Received May 1, 1973

A nonmetal template synthesis of bis(β -imino amine) macrocycles possessing 14-, 15-, and 16-membered rings has been devised. The method is based on the electrophilic reactivity of 1,2-dithiolium cations and vinylogous β -amino thiones with primary amines. The 4-phenyl-1,2-dithiolium cation with ethylenediamine and trimethylenediamine yields the precursor bis(β -amino thiones) **20** and **21**. These compounds are smoothly cyclized by reaction with diamines to afford the 14- and 16-membered macrocycles **24** and **26**, respectively, in high yield. The 15-membered cycle **25** was obtained in lower yield from **21** and ethylenediamine. Reaction of the amino thione complex **23** with trimethylenediamine results in formation of metal-free **26** in good yield by an apparent template process. Ring closure could not be effected by reaction of diamines with the bis(β -amino thiones) obtained from the 3-phenyl-1,2-dithiolium cation, indicating that this method of macrocyclic synthesis is best applied to precursors containing thioaldehyde groups. $Cu(II)$, $Ni(II)$, and $Co(II)$ complexes of the three macrocycles were prepared. The development of a nontemplate synthesis of macrocycles was undertaken because of the inability to extend a previous reaction sequence yielding **15** from **12** and ethylenediamine to the synthesis of larger tetraaza ring systems. Alternative preparations of **15** are described. The nontemplate approach allows the synthesis of series of macrocyclic complexes of the basic chelate ring-size patterns 1-3 with the desired sets of metal ions. Together with the template cyclization reactions originated by Jager and the recently reported reactivity features of the β -imino amine chelate rings, it affords entry to a broad variety of tetraaza macrocyclic systems.

Introduction

Central to the problem of understanding the structural, electronic, and reactivity properties of natural and synthetic tetraaza macrocyclic complexes is an elucidation of the effects of chelate ring size and ligand rigidity and extent of unsaturation on these properties. Of the six ring-size patterns generated by fusion of four five- and/or six-membered chelate rings, those of the 6-5-6-5, 6-5-6-6, and 6-6-6-6 types, represented schematically by **1**, **2**, and **3**, respectively, are of



pertinence here. Patterns **2** (corrins) and **3** (porphyrins) are the only types found in natural macrocycles whereas all three

(1) National Science Foundation predoctoral fellow, 1970-1973.