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Vibrational Spectra of Thiosemicarbazide Complexes of Copper(II), Nickel(II), Palladium(II), and Platinum(II) and the Use of the Metal Isotope Natural Abundance in Their Assignment together with Supporting Evidence from Incoherent Inelastic Neutron Scattering Spectroscopy

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Infrared and Raman spectra from 600 to 200 cm^{-1} of the thiosemicarbazide complexes $M(NH_2NHCSNH_2)_2X_2$ [where M = Cu(II), Ni(II), Pd(II), and Pt(II) and X = Cl, Br, and also I in the case of Pd(II) and Pt(II)], $M(NH_2NCSNH_2)_2$ [where M = Ni(II) and Pd(II)], and $Ni(NH_2NHCSNH_2)_3X_2{\cdot}H_2O$ (infrared only) (where X = Cl or Br) have been obtained, together with the complexes in which the ligand hydrogen atoms have been replaced by deuterium. All the bis complexes studied have been shown to have the trans square-planar structure. A vibrational assignment has been made on this basis with the bands due to ν_{M-N} and ν_{M-S} identified in the infrared and Raman spectra. Splittings due to the metal isotope natural abundance have been observed and used in the assignment of the ν_{M-S} modes. Incoherent inelastic neutron scattering spectra of $M(NH_2CHCSNH_2)_2Br_2$, where M = Cu(II) and Ni(II), confirm the above assignments. These assignments markedly modify those in the current literature.

Introduction

Thiosemicarbazones have been shown to be pharmacologically active against viruses, protozoa, smallpox, and certain kinds of tumors and have been suggested as possible pesticides and fungicides.[1] The active species is found not to be the thiosemicarbazone itself but a metal chelate of thiosemicarbazone.[2] The vibrational spectra of some chelate complexes formed by thiosemicarbazide (Htsc) (which could be considered as the simplest member of the thiosemicarbazones) are the subject of the present investigation.

The complexes formed by thiosemicarbazide with transition metals are first reported by Jensen.[3] Since then, a number of complexes of this ligand with a variety of metals have been characterized.[4–8] X-ray crystallographic analysis of some of these complexes show the ability of thiosemicarbazide to behave both as a mono- and a bidentate ligand.[9–13] Mid-infrared spectral assignments have been reported for the thiosemicarbazide ligand itself[14] and for the complexes formed with Cu(II), Ni(II), Ag(I), Zn(II), Cd(II), and Hg(II).[4,7,15]

There are several reports of the far-infrared spectra of these complexes giving incomplete tentative assignments of the metal–ligand vibrations,[4,16] and two groups of workers have reported normal-coordinate analyses[17] of the in plane modes of $Ni(Htsc)_2Cl_2$ and $Ni(tsc)_2$. There appears to be several large unsystematic discrepancies between the reported spectral infrared frequencies of these two sets of reports. Our observed infrared frequencies agree well (except for a systematic error of two wavenumbers) only with those reported for $Ni(Htsc)_2Cl_2$ by Geetharani et al.[17a] Our deuterations which are almost complete (checked against the NH stretching region in the infrared) show frequencies very different from those of earlier workers, thus challenging the validity of the results of their normal-coordinated analyses. There is therefore a need for a reinvestigation of the metal–ligand stretching region so as to obtain reliable metal–ligand vibrational assignments for these complexes.

Experimental Section

All the complexes were prepared by the methods described in the literature.[3,4,6] $Ni(Htsc)_2X_2$ (where X = Cl or Br) was also prepared by mixing almost saturated aqueous solutions of $NiX_2{\cdot}6H_2O$ and thiosemicarbazide at 80 °C in the molar ratio 1:2 when the required complex precipitates as a dark green solid.

The complexes thus formed show infrared spectra, elemental analysis, and x-ray powder photographs identical with those prepared by literature methods.[4] This method was used for the preparation of the deuterium analogoues as it gave almost complete deuteration with comparative ease compared to literature methods.[4] The ligand itself was first detuerated by repeated recrystallizations from deuterium oxide. The deutero analogoues were prepared by using deuterated solvents and reagents in the above preparations. All the complexes were checked by elemental analysis and their mid-infrared spectra.

Infrared spectra from 600 to 200 cm^{-1} were obtained with a Perkin-Elmer 325 infrared spectrophotometer at a resolution of approximately 1.5 cm^{-1} and from 400 to 40 cm^{-1} on an RIIC Fourier spectrophotometer FS-720 at a resolution of 2.5 cm^{-1}. Spectra where higher resolution was used are indicated in the text. Samples were examined as Nujol mulls on polyethene plates. Raman spectra of the polycrystalline samples were obtained on a Spex Raman spectrophotometer Model 1401 equipped with a Model 165 ion laser. A rotating Raman cell similar in construction to that reported by Kiefer and Bernstein[18] was used to obtain the Raman spectra of the highly colored complexes in order to minimize thermal decomposition.

Neutron-scattering experiments were carried out with the beryllium-filter detector spectrometer[25] at AERE (DIDO), Harwell.

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Table I. Vibrational Spectra[a] of Bis(thiosemicarbazide) Complexes

	$Cu(Htsc)_2Cl_2$				$Ni(Htsc)_2Cl_2$				$Pd(Htsc)_2Cl_2$					$Pt(Htsc)_2Cl_2$				
band[b]	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	assignt
1	461	429	32	06	523	500	23	00	496	472	24	00		510	483	27	05	ν(M-N)
									460									
2	429	399	30	02	436	417	19	02	430	403	27	01		438	412	26	04	ligand, in-plane def
3	320	306	14	02	338	321	17	02	330	317	17	03	05	322	304	18	04	δ(M-N-N)
									312	304	08	01	04					combination
4	287	283	04	01	378	362	16	02	305	290	15	03	08	298	292	06	05	ν(M-S)
5	263	232	31	22	288	251	37	19	277	242	35	15	44	292	255	37	41	ligand, out-of-plane def + lattice mode

	$Cu(Htsc)_2Cl_2$		$Ni(Htsc)_2Cl_2$				$Pd(Htsc)_2Cl_2$					$Pt(Htsc)_2Cl_2$				
band[c]	NH	$\Delta\nu_2$	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	NH	ND	$\Delta\nu_1$	$\Delta\nu_3$	assignt
1	448	05	491	461	30	04	500	472	28	01	02	535	510	25	01	ν(M-N)
			478	411		01	467			08		520	492	28	16	
							450	431	19		00	493	459	34	13	
2	428	03	434	397	37	04	440	410	30	02	02	451	424	27	03	ligand
3		318*	321				353	332	21	05	07	322	300	22	02	δ(M-N-N) + ν(M-S)
4	246	01	298	281	17	03	304	287	17	02	04	340	324	16	06	ν(M-S) + δ(M-N-N)
5	218	06	237	234	03	241*	226	224	02	02	03	239	236	03	03	δ(M-S-C)
			225	216	09	232*										

[a] Key: $\Delta\nu_1$, deuteration shift; $\Delta\nu_2$, anion substitution (Cl/Br) shift; $\Delta\nu_3$, anion substitution (Cl/I) shift; *, actual frequency of the bromide. [b] Far-infrared spectra in the metal–ligand stretching region of bis(thiosemicarbazide) complexes and their deuterio analogues together with the anion substitution shifts (frequencies quoted in cm^{-1}). [c] Raman spectra in the metal–ligand stretching region of bis(thiosemicarbazide) complexes and their deuterio analogues together with the anion substitution shifts (frequencies quoted in cm^{-1}).

Polycrystalline samples in aluminium sachets were used and spectra run around 10 K. Thiosemicarbazide, nickel(II) halides, and copper(II) halides were purchased from the British Drug House Ltd. K_2PtCl_4 and K_2PdCl_4 were purchased from Johnson Matthey Chemicals Ltd. and used directly without further purification. Deuterium chloride and bromide were purchased from CIBA and ammonium-d_4 hydroxide from Prochem B.O.C.

Results and Discussion

This investigation concerns mainly the assignment of the metal–ligand stretching vibrations of these complexes. These together with the ring skeleletal deformations and lattice modes appear mainly in the region below 600 cm^{-1}. Lattice modes are mainly confined to a region below 150 cm^{-1}.[19] The following assignment is based on deuterium substitution, anion substitution, comparisons within this series of complexes and other related compounds, and the splittings due to the metal-isotope natural abundance.[20] The vibrational modes are assigned to the observed bands to which, in our opinion, they contribute predominantly. Incoherent inelastic neutron scattering spectroscopy, which provides a hydrogen amplitude weighted density of states spectrum,[26] has been used in support of our assignments.

Bis(thiosemicarbazide)metal(II) Dihalide Complexes. The infrared and Raman spectra of $M(NH_2CSNHNH_2)Cl_2$, where M = Cu(II), Ni(II), Pd(II), and Pt(II), in the 600–200-cm^{-1} region are shown in the form of a line diagram in Figure 1, and their frequencies together with those of their deuterio analogues ($NH_2CSNHNH_2 \rightarrow ND_2CSNDND_2$) and the band shifts observed on anion substitution are give in Table I. The centrosymmetric, trans square-planar structure of this cation $Ni(Htsc)_2^{2+}$ shown by X-ray crystallography to exist in many of its salts,[10,11] manifests itself in the lack of coincidences between vibrational modes in the infrared and the Raman spectra. With complex spectral patterns it is reasonable to expect occasional accidental coincidences.

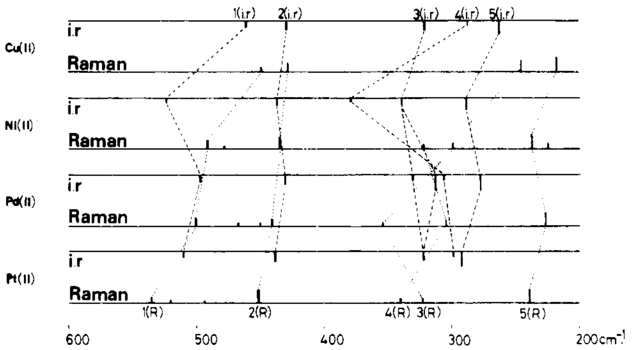

Figure 1. Comparison of the vibrational spectra of the dichlorides of bis(thiosemicarbazide) complexes of Cu(II), Ni(II), Pd(II), and Pt(II).

X-ray powder photographs of all the complexes studied including their deuterio analogues were obtained. A comparison of these photographs showed them to have very similar intensity patterns, thus indicating the probable similarity of the crystal structures of all these complexes. This justifies a comparison of the spectra of these complexes in the following assignment.

Bands in the spectra are numbered 1 to 5 in the line diagram (Figure 1) from high frequency to low frequency. Deuteration shifts for $C(Htsc)_2Cl_2$ in the Raman are not available, and hence the assignment of the Raman spectrum of this compound is made by comparison with those of the other complexes.

In these bis(thiosemicarbazide) complexes (structure 1), clearly all the vibrational modes involving the movement of any of the nitrogen atoms will be sensitive to deuterium substitution of the ligand. Therefore, in the cases of $Cu(Htsc)_2Cl_2$ and $Pt(Htsc)_2Cl_2$, the bands in the infrared at 287 and 298

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(20) (a) Deuterium substitution is expected to shift hydrogenic vibrations. Frequency shifts for nonhydrogenic vibrational modes would depend on their proximity to hydrogen atoms. In spite of extensive coupling expected for compounds with chelate ring systems, significant effects are still observed; for example, ν(M–S) shows the least shifts while ν(M–N) the largest as expected, apart from an out of plane deformation mode which involves a considerable NH movement (Table I). (b) Anion substitution is useful in assigning vibrations which are appreciably mixed with lattice modes.[19] (c) A comparison of a structurally similar series of complexes with the same ligand but with different metal atoms could often provide with a distinction between the metal–ligand modes and those confined to the chelate ring. (d) Splittings of bands due to metal–isotope natural abundance:[21] here one looks for a metal isotope splitting with a frequency difference and an intensity ratio calculable from the metal–isotope natural abundance. With these stringent requirements, it is expected that one would be able to distinguish these splittings from solid state effects like factor group and site group splittings. (e) Incoherent inelastic neutron scattering spectroscopy:[26] this gives a clear picture of the normal modes involving hydrogen motions.

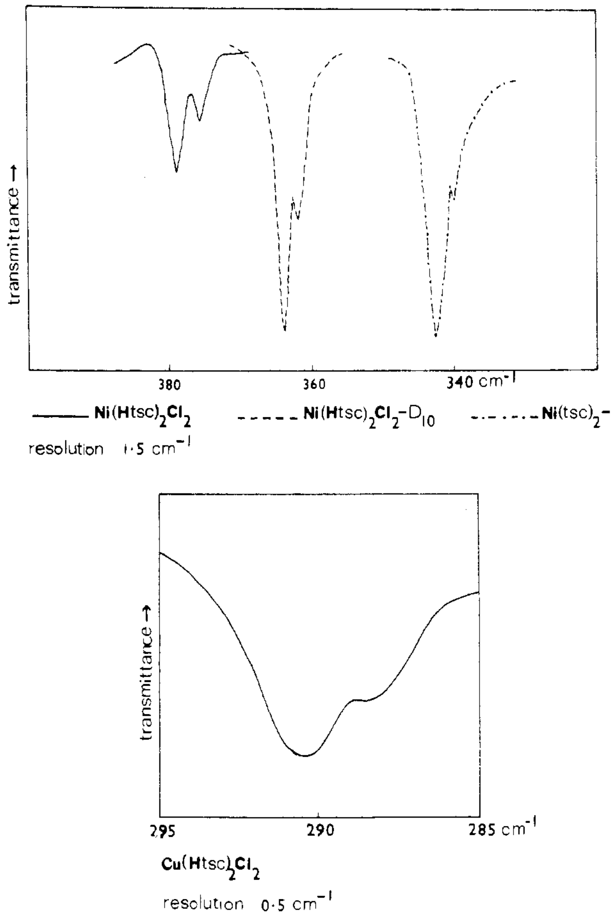


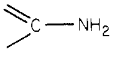
Figure 2. Metal-isotope natural abundance splittings in the bands assigned to the metal–sulfur stretches. Spectra were run at liquid-nitrogen temperature.

cm^{-1}, respectively, being the least sensitive to deuterium substitution can be assigned to be predominantly due to the metal–sulfur stretching modes (band 4; IR).

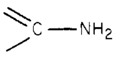
The metal-isotope natural abundance of copper being 69.09% of ^{63}Cu and 30.91% of ^{65}Cu, it should be possible to observe the splitting of the ν(Cu–S) mode, similar to that reported for the ν(Ni–S) mode in bis(β-mercaptoethylamine)nickel(II).[21] In fact a spectrum run at liquid-nitrogen temperature and at a resolution of 0.5 cm^{-1} (Figure 2) showed a clear shoulder on the low-frequency side of the band already assigned to the ν(Cu–S) mode. The splitting observed is about 2 cm^{-1} and with an approximate intensity ratio in agreement with the copper isotope natural abundance, thus confirming the assignment of ν(Cu–S). It should be mentioned that there are no significant changes in the low-frequency spectrum on cooling, showing the absence of any phase changes.

Band 5 (IR) of these complexes show very high deuterium sensitivity, suggesting an assignment to a vibrational mode confined to the ligand. However, this also shows by far the biggest shift with anion substitution, indicating a high degree of mixing with a lattice mode. In fact, this band shows very similar behavior to a band in the same frequency region in bis(ethylenediamine) complexes,[19] which has been reliably assigned to a chelate ring out of plane deformation coupled to a lattice vibration. Therefore, we disagree with the interpretations of earlier workers[17] who have assigned this mode to a predominantly metal–sulfur bond stretching vibration, and we assign it to a mixture of the out of plane chelate ring deformation and a lattice mode. The metal–nitrogen bending mode δ(M–N–N), which by analogy with other similar complexes should appear in this region, is assigned tentatively to the bands at 320 and 322 cm^{-1} in the infrared spectra of these complexes of Cu(II) and Pt(II) respectively (band 3; IR).

The higher frequency end of this region (400–550 cm^{-1}) shows a consistent patten of two bands for each of the four complexes (bands 1 and 2; IR). The deuteration shifts cannot be made use of in distinguishing between these two modes as they both show similar shifts. This is expected as these two are probably a metal–nitrogen stretching and a ligand mode. However, in going down the series of complexes Cu(II), Ni(II), Pd(II), and Pt(II), band 2 (IR) remains almost unchanged in frequency while band 1 (IR) shows appreciable sensitivity toward a change of the metal atom. Therefore, band 1 (IR) is assigned to the metal–nitrogen stretching frequency as this mode would be more sensitive to a change of the metal atom, whereas a mode confined to the ligand, involving probably the bending



group would be less sensitive. In fact, a normal-coordinate analysis reported for a related compound, thioscarbohydrazide, gave an assignment of a band at 469 cm^{-1} to the



deformation.[15] These two modes have the same symmetry (both in-plane modes) and hence liable to be coupled together, with the extent of coupling determined by the frequency separation. This is immediately apparent if one were to consider the relative intensities of these bands. The metal–nitrogen stretch 1 (IR), which is relatively weak in intensity in the Ni, Pd, and Pt complexes, becomes relatively strong in the case of the Cu complex by stealing intensity from band 2 (IR) whose separation from band 1 (IR) is the smallest within this series of complexes (Figure 4).

The assignment of the metal–sulfur stretching vibration of the nickel(II) complex is more complicated. A comparison with the other complexes shows band 3 (IR) and 4 (IR) to be the probable candidates for this mode. However, both these bands show fairly large deuteration shifts of similar magnitude, suggesting a strong mixing of these two modes. A high-resolution spectrum of Ni(Htsc)$_2$Cl$_2$ at liquid-nitrogen temperature shows a splitting of only band 4 (IR) by about 3 cm^{-1} (Figure 2), with an intensity ratio which is in agreement with the nickel-isotope natural abundance. No appreciable change in the band pattern of the low-frequency region is observed on cooling, indicating the absence of any phase change. The splitting observed in band 4 (IR), being comparable to that observed in the case of bis(β-mercaptoethylamine)nickel(II) complex, which has a relatively uncoupled nickel–sulfur stretching mode,[21,22] suggests an assignment of a relatively pure metal–sulfur stretch to band 4 (IR) compared to that in the deuterio complex. The exceptionally large deuteration shift of this band is understood by studying the metal-isotope natural abundance splitting of the corresponding band in the deuterio analogue, where the splitting is reduced to about 2 cm^{-1} (Figure 2). This is a substantial reduction which cannot be accounted for by only the frequency shift on deuteration. This could be explained if band 2 (IR) comes farily close to band 4 (IR) in frequency on deuteration, thus interacting with it and splitting each other apart in frequency, so that band 4 (IR) is assigned to have a larger proportion of the nickel–sulfur stretch in the case of the protonated species compared to that in the deuterio analogue. This explanation assumes the sym-

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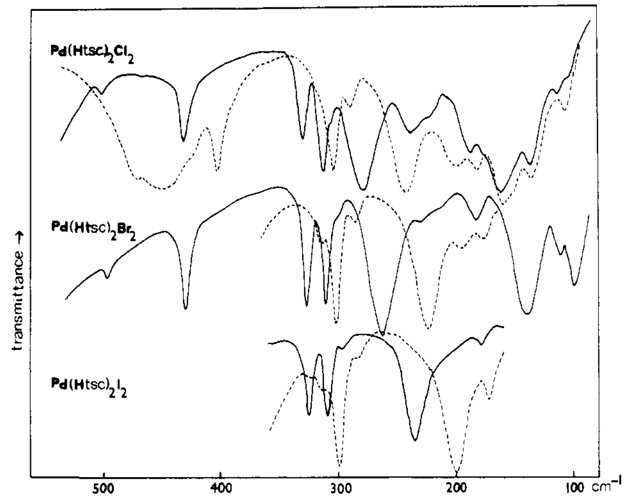
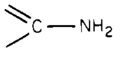


Figure 3. Far-infrared spectra of the bis(thiosemicarbazide) complexes of palladium(II) and their deuterio analogues (dotted lines).

metries of the two modes corresponding to bands 2 (IR) and 4 (IR) to be the same. This is reasonable when the earlier suggestion of a ligand mode involving the



group, an in-plane deformation, is considered as the origin of band 2 (IR). This interaction also explains the significantly low deuteration shift of the band 2 (IR) in $Ni(Htsc)_2Cl_2$ compared to those in the other complexes.

The metal–sulfur stretching region in the case of the Pd(II) complex poses further complications with an additional band appearing, thus giving rise to two strong and one weak band. On deuteration the higher frequency strong band almost disappears. The same effect is observed on deuterating the bromide and the iodide (Figure 3). This peculiarity could be explained by invoking strong Fermi resonance between a mode in this region and an overtone or a combination, in the case of the protonated species, which diminishes considerably in strength on deuteration when the bands concerned shift apart. The metal–sulfur stretching bands so far assigned to these complexes have been consistently of lower intensity than the other bands in this region. By such a comparison the weakest band of these three in the Pd(II) complex could be tentatively assigned to the palladium–sulfur stretching mode. As this is the only compound in the series to show this extra band (Figure 3 and 4), it is unlikely to arise from factor group or site effects especially as it disappears on deuteration.

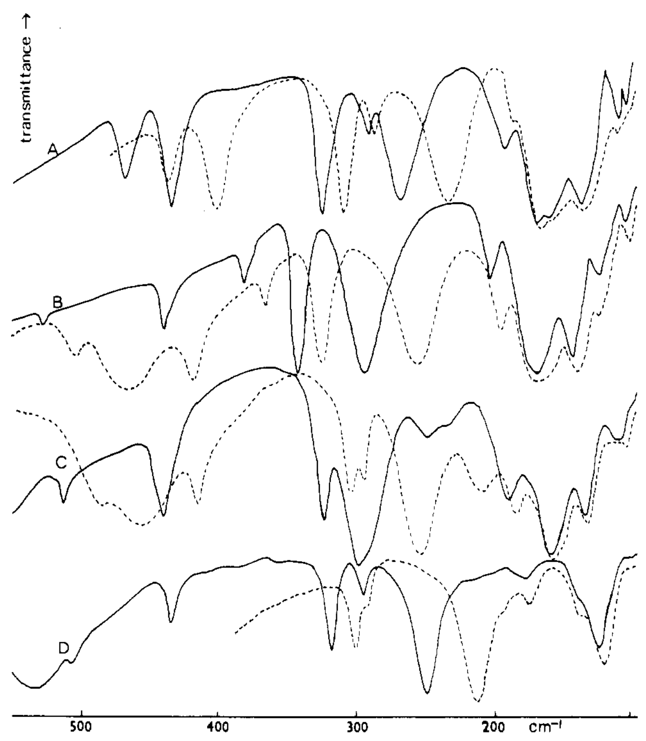


Figure 4. Far-infrared spectra of (A) $Cu(Htsc)_2Cl_2$, (B) $Ni(Htsc)_2Cl_2$, (C) $Pt(Htsc)_2Cl_2$, (D) $Pt(Htsc)_2I_2$, and their deuterio analogues (dotted lines).

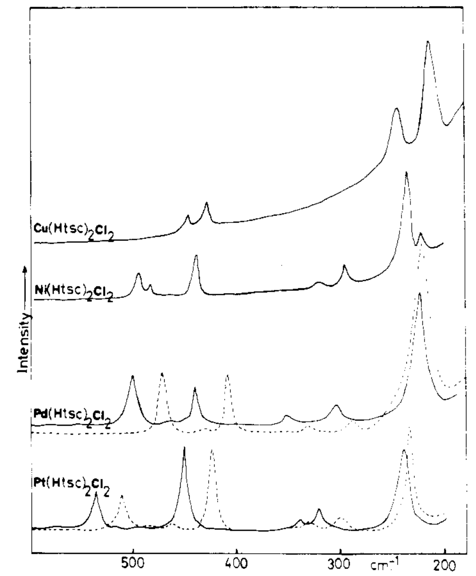


Figure 5. Raman spectra of bis(thiosemicarbazide) complexes of Cu(II), Ni(II), Pd(II), and Pt(II) and their deuterio analogues (dotted lines).

Raman spectra of these complexes are shown in Figure 5, and their frequencies are given in Table I. At the higher frequency end (400–600 cm^{-1}), there are two relatively strong bands showing a similar pattern of perturbations with deuterium and anion substitution and with a change of the central metal atom as shown by the corresponding bands in the infrared. Consequently these two bands are assigned to the Raman-active counterparts of bands 1 (IR) and 2 (IR). There are one or two highly deuterium-sensitive weak features in this region depending on the complex that are probably due to overtones and combinations. The bands numbered 4 (R) and 3 (R) show similar deuterium shifts and are assigned to the symmetric metal–sulfur stretch and the metal–nitrogen deformation, strongly coupled together. Note the drastic reduction of this coupling in the case of $Ni(tsc)_2$(vide infra), where the introduction of a double bond into the chelate ring moves these modes too far apart to interact appreciably. The strong Raman band 5 (R), which is comparatively insensitive to deuterium as well as anion substitution, is probably the metal–sulfur in-plane deformation δ(M–S–C). These assignments of bands 4 (R) and 5 (R) to in-plane vibrations having the sulfur atom in common is in good agreement with the comparatively large intensity of band 4 (R) in the case of the Cu(II) complexes where the frequency separation between these modes is the smallest compared with the other complexes in this series. The Raman spectra of the highly colored Cu(II) complexes on comparison with those of the other complexes indicate the absence of a weak band that was assigned to have the metal–nitrogen deformation δ(M–N–N) as the main contributor.

In principle all vibrations, whether IR or Raman active, are observable in the incoherent inelastic neutron scattering (IINS) spectrum. However, intensity of these vibrations in the IINS is determined by the incoherent neutron scattering cross section of the vibrating atoms and their amplitudes of motion in the

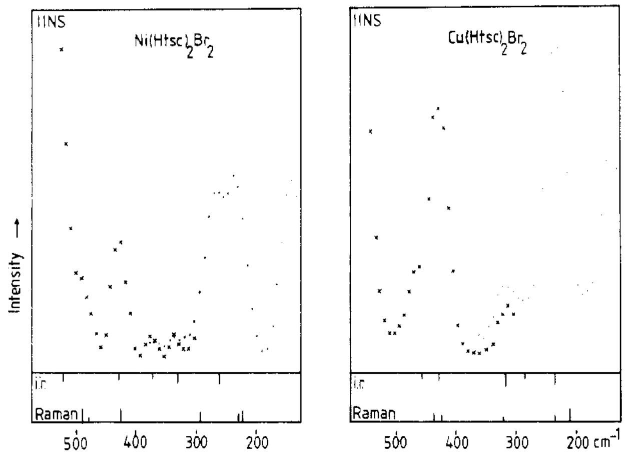


Figure 6. Comparison of the incoherent inelastic neutron scattering spectra with IR and Raman spectra of $Ni(Htsc)_2Br_2$ and $Cu(Htsc)_2Br_2$: (···) aluminum (111) and (*) aluminum (311) planes of the monochromator.

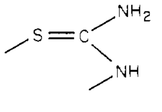
Table II. Incoherent Inelastic Neutron Scattering Spectra in the Metal-Ligand Stretching Region of the Bis(thiosemicarbazide) Complexes (Frequencies Quoted in cm^{-1})

$Cu(Htsc)_2Br_2$	$Ni(Htsc)_2Br_2$	assignt
471	490	ν(M-N)
426	430	ligand in plane def
	370	ν(M-S)
315	338	δ(M-N-N)
238	271, 242	ligand out-of-plane def + lattice mode

normal mode. The fact that the incoherent neutron scattering cross section of hydrogen is by far the largest, greater than for any other element by a factor of about 10, and the large amplitude of motion of the hydrogen atoms in the normal mode due to its very small mass makes the IINS spectrum of a hydrogen containing material to be dominated by the normal modes involving the motion of hydrogen atoms.[26] Therefore, in IINS spectroscopy one observes the hydrogen-amplitude-weighted density of state spectrum of the sample. Figure 6 shows the IINS spectra of $Cu(Htsc)_2Br_2$ and $Ni(Htsc)_2Br_2$ together with stick diagrams of the IR and Raman spectra of these complexes. IINS frequencies are given in Table II. The bromides were chosen for this particular experiment because the vibrational frequencies are better separated than in the case of the chlorides and hence assist in easy resolution of the bands in the IINS spectrum, which has very much poorer resolution as compared with IR or Raman techniques.

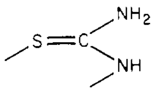
A comparison of the IR and Raman spectra of the Ni(II) complex with its IINS spectrum makes immediately apparent the prime candidacy of the vibrations corresponding to the bands at 378 and 338 cm^{-1} (showing only a little intensity and hence very little hydrogen movement in the respective normal modes) to the metal–sulfur stretching mode in good agreement with our assignment. Furthermore the IINS spectrum shows a very high intensity for the band at 270 cm^{-1}, thus indicating a high amplitude of hydrogen motion in this normal mode, and is, therefore, in complete disagreement with the assignment of a predominantly metal-sulfur stretching character to this mode by the earlier workers.[17]

Following is a qualitative explanation of the IINS intensities based on the assignments we have so far proposed. The strongest IINS bands in this region are those assigned to ligand in-plane deformation of an $-NH_2$ group, i.e.



and a ligand out-of-plane deformation, i.e., ring pucker, together with a contribution from a lattice mode. Clearly these modes involve considerable hydrogen amplitude of motion to justify their intensities in the IINS.

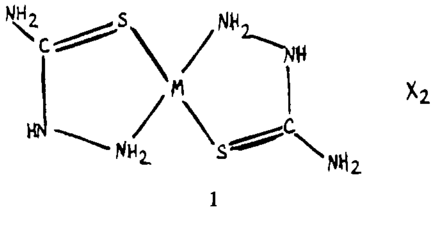
Next in intensity are those assigned to the metal–nitrogen stretch where the intensity would be due to the hydrogens riding on the nitrogen atom in this normal mode. The least intense bands in the IINS are those assigned to δ(M–N–N) and ν(M–S). The low intensity of the above metal–nitrogen deformation could be rationalized if one were to visualize the form of this vibration as a deformation about the NH_2 group, thus making this group almost stationary with the intensity being provided by the solitary hydrogen attached to the other nitrogen atom. Also the possible mixing of this vibration with that assigned to the deformation of the



group (band 2; IR) cannot be overlooked.

The presence of comparable intensity in the band assigned to ν(M–S) to that of δ(M–N–N) in the case of the Ni(II) complex would most probably be due to the mixing of ν(M–S) with the ligand deformation (band 2; IR). The frequency differences between the vibrations 2 (IR) and 3 (IR) do not vary much in this series of complexes [Cu(II), 109 cm^{-1}; Ni(II), 98 cm^{-1}; Pd(II), 100 cm^{-1}; Pt(II), 116 cm^{-1}], thus showing similar mixing between these modes in the complexes while the frequency separations between vibrations 2 (IR) and 4 (IR) [Cu(II), 142 cm^{-1}; Ni(II), 58 cm^{-1}; Pd(II), 125 cm^{-1}; Pt(II), 160 cm^{-1}] show a distinct difference in the case of the Ni(II) complex where the separation is less than half that found in other complexes, thus indicating the liklihood of stronger mixing. The absence of IINS intensity in the band assigned to the metal–sulfur stretch (band 4; IR) in the Cu(II) complex is in good agreement with the above assignment of a normal mode mainly localized on the metal–sulfur bond in this complex.

Bis(thiosemicarbazido)metal(II) Complexes. A neutral nickel complex which is very close in structure to the complex cation in bis(thiosemicarbazide)nickel(II) dihalides is bis(thiosemicarbazido)nickel(II). These thiosemicarbazido complexes too were first reported by Jensen,[3] and later Haines and Sun[6] repeated the preparations. Cavalca et al.[12] have determined the structure of this complex by X-ray crystallography. A trans arrangement of the thiosemicarbazide ligands was shown to be present and the loss of a proton from the middle nitrogen indicated (structure **2**). It is of interest



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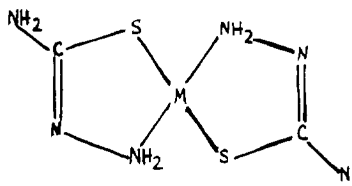

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Table III. Vibrational Spectra of Bis(thiosemicarbazido) Complexes[a]

	$Ni(tsc)_2$			$Pd(tsc)_2$			
band[b]	NH	ND	$\Delta\nu_1$	NH	ND	$\Delta\nu_1$	assignt
1	528	510	18	499	474	25	ν(M-N)
	470	487		480	456	24	
				458			
2	439	423	16	435	427	8	ligand
					412		
3	388	368	20	362	341	21	δ(M-N-N)
				349			
4	346	340	6	315	310	5	ν(M-S)
5	297	250	47	252	226	26	ligand
	255	227	28				

	$Ni(tsc)_2$			
band[c]	NH	ND	$\Delta\nu_1$	assignt
1	569	534	35	ν(M-N)
2	495	469	27	ligand
3	427	400	27	δ(M-N-N)
4	326	326	00	ν(M-S)
5	303	290	13	ligand
	237	231	06	δ(M-S-C)

[a] $\Delta\nu_1$ = deuteration shift. [b] Far-infrared spectra in the metal-ligand region of bis(thiosemicarbazido) complexes and their deuterio analogues. [c] Raman spectra of bis(thiosemicarbazido)nickel(II) and its deuterio analogue.

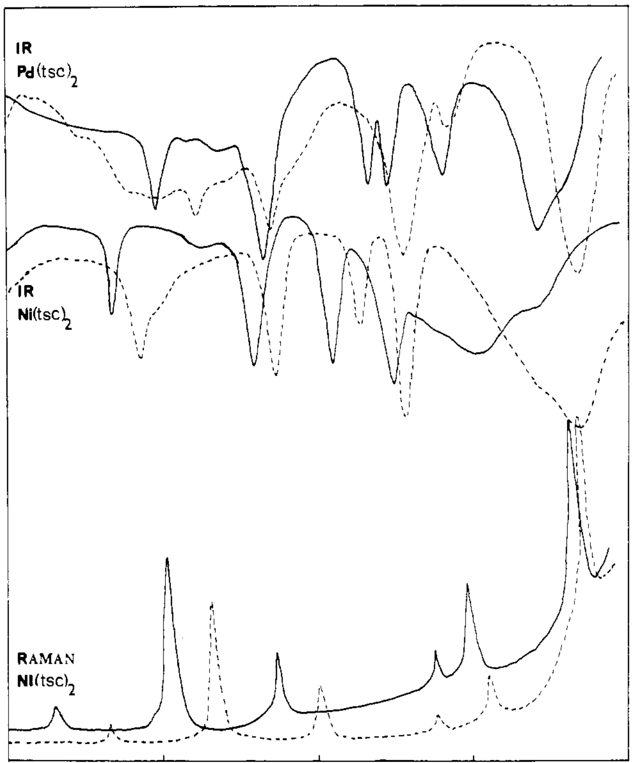


Figure 7. Vibrational spectra of bis(thiosemicarbazido)nickel(II) and -palladium(II) and their deuterio analogues (dotted lines).

to note that the metal–sulfur and metal–nitrogen bond distances in this compound are similar to those reported for bis(thiosemicarbazide)nickel(II) cation in many of its salts.[10,11]

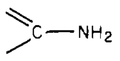
Infrared and Raman spectra of this compound together with its deuterio analogue are given in Figure 7, and their frequencies are given in Table III. The absence of infrared and Raman coincidences for this complex, $Ni(tsc)_2$, is in agreement with the presence of a center of symmetry in its structure. The spectra have been assigned by comparison with those of the bis(thiosemicarbazide)metal complex cations and with the help of the deuteration shifts observed.

The bands least sensitive to deuteration are at 346 and 326 cm^{-1} in the infrared and Raman spectra, respectively. These are thus assigned to be predominantly due to the nickel–sulfur asymmetric and symmetric stretches, respectively. It is noticed that the metal–nitrogen deformations δ(M–N–N), have increased in frequency in the IR and the Raman in going from $Ni(Htsc)_2Cl_2$ to $Ni(tsc)_2$. This is to be expected as this deformation would involve a large contribution from the deformation of the ligand skeleton, and consequently the introduction of a double bond between the carbon and nitrogen in the ligand ring would demand more energy for its deformation. The large increase in frequency of this mode in the Raman has left an almost uncoupled metal–sulfur stretch (almost zero deuterium shift) in contrast to what is observed in the case of the complex cations (vide supra). There are two rather broad bands in the infrared at 296 and 255 cm^{-1} that are very sensitive to deuteration and are assigned to ligand modes. A band in the Raman at 237 cm^{-1} is relatively insensitive to deuteration (shift 6 cm^{-1}) and is probably the metal–sulfur deformation δ(M–S–C).

Metal–nitrogen stretching modes are assigned to the bands at 528 and 569 cm^{-1} in the infrared and the Raman, respectively. These bands are of high sensitivity toward deuteration, and this assignment is in agreement with those of bis(thiosemicarbazide) complex cations. The ligand modes that are assigned to bands 2 (IR) and 2 (R) in the bis(thiosemicarbazide) complex cations are probably those at 439 and 427 cm^{-1}, respectively, in the infrared and Raman spectra of this complex.

In the protonated complex $Ni(tsc)_2$, the splitting due to the nickel-isotope natural abundance is not observed probably due to the band assignable to the metal–sulfur stretch being overlapped by a broad band due to a ligand skeletal mode (Figure 7). However, in the deuterio analogue a definite shoulder can be seen on the band assigned to the metal–sulfur stretch with a splitting of about 3 cm^{-1} and the expected intensity distribution when a spectrum is run at liquid-nitrogen temperature (Figure 2). This confirms the assignment of the metal–suflur stretching mode in this complex.

The comparison of the band frequencies in the spectra of $Ni(tsc)_2$ with those of $Ni(Htsc)_2Cl_2$ is in good agreement with that expected. Metal–sulfur and metal–nitrogen stretching modes change only a little in frequency while an in-plane deformation involving the metal–nitrogen bond and the chelate ring changes appreciably in frequency. It is also interesting to note the mode which was assigned to a deformation of the



group remaining almost unchanged in frequency, thus confirming our assignment.

A spectrum similar to that for the bis(thiosemicarbazide)palladium(II) cation was observed for the related compound bis(thiosemicarbazido)palladium(II) (Figure 7). Table III gives a tentative assignment of the infrared spectrum of this compound from the deuteration shifts observed and by a comparison with the other complexes studied. The band in the infrared at 315 cm^{-1} which has the least deuteration shift (5 cm^{-1}) is assigned predominantly to the palladium–sulfur stretching mode. The fact that the two bands of almost equal intensity at 362 and 349 cm^{-1} in the protonated complex are replaced by a band at 341 cm^{-1} in the deuterated complex with about twice the intensity of either of the former bands is in good agreement with the suggestion of Fermi resonance between an overtone or combination band with the δ (Pd–N–N) mode in this complex as in the case of bis(thiosemicarbazide)palladium(II) cation. A comparison of the spectra of this complex with those of $Pd(Htsc)_2Cl$ shows the band assigned to δ(Pd–N–N) mode increases in frequency (40 cm^{-1})

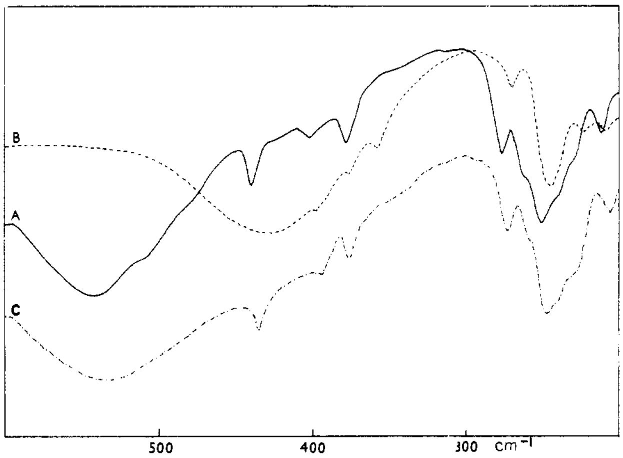


Figure 8. Far-Infrared spectra of (A) $[Ni(Htsc)_3]Cl_2 \cdot H_2O$, (B) its deuterio analogue, and (C) its bromide.

Table IV. Far-Infrared Spectra of Tris(thiosemicarbazide)nickel(II) Dichloride Hydrate and Its Deuterio Analogue[a]

NH	ND	$\Delta\nu_1$	$\Delta\nu_2$	assignt
540	440	100	10	
439			3	ligand
400	375	25	4	ν(M-N)
376	354	22	2	ν(M-N)
274	268	6	3	ν(M-S)
260			2	
248	242	6	3	ν(M-S)
238	222	16	8	ligand
210	208	2	5	

[a] $\Delta\nu_1$ = deuteration shift, $\Delta\nu_2$ = anion substitution (Cl/Br) shift.

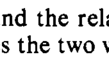
in this complex while that assigned to ν(Pd–S) remains relatively unmoved. This observation is similar to that observed in the case of the nickel(II) complexes and is in agreement with the structural differences between these two ligands. The fact that the δ(Pd–N–N) mode is well removed in frequency from ν(Pd–S) in this complex provides a clearer picture of the intensity changes taking place on deuteration.

In all the complexes discussed it is noted that the NH_2 rocking mode moves down in frequency to the region below 600 cm^{-1} upon deuteration. It is interesting to note that this does not appear to interact with the other vibrational modes in this region (600–400 cm^{-1}), and in fact these bands cross each other in several of the complexes on deuteration. This agrees with the assignment of the two modes in this region to the metal–nitrogen stretch and an in-plane skeletal deformation of the ligand. The NH_2 rock, being an out-of-plane mode, is symmetry forbidden to interact with these modes.

Tris(thiosemicarbazide)nickel(II) Dichloride Hydrate. An X-ray crystallographic analysis of tris(thiosemicarbazide)-nickel(II) dichloride hydrate has shown it to have the nickel atom in the complex cation in a distorted octahedral geometry surrounded by three sulfur atoms and three nitrogen atoms.[23] It is also shown to be the meridianal isomer. This tris compound was originally reported by Jensen.[3]

The far-infrared spectra of this compound together with that of its bromide and its deuterio analogue are shown in Figure 8. The deuteration and anion substitution shifts together with a comparison of these spectra with those of the bis(thiosemicarbazide) complexes are used to arrive at the assignment given in Table IV.

The two bands in the infrared at 274 and 248 cm^{-1} which are the least perturbed by deuteration are assigned to the metal–sulfur stretching modes. Three bands are formally allowed for this symmetry but one of these is not observed and is probably very weak in intensity. A comparison of the upper end of this region of this spectrum with those of the bis(thiosemicarbazide) complexes shows the presence of a band corresponding to that assigned to a deformation of the



group. Its frequency, which is almost the same as that assigned in the bis complexes, and the relative intensity support this assignment. This leaves the two weak bands at 376 and 400 cm^{-1} with appreciable deuterium sensitivity to be assigned to the metal–nitrogen stretching modes. The lowering of the metal–ligand frequencies by about 100 cm^{-1} in going from the bis complexes to the tris complexes is in good agreement with

Table V. Summary of the Metal-Ligand Stretching Frequencies

complex	ν(M-S) IR	ν(M-S) Raman	ν(M-N) IR	ν(M-N) Raman
$Cu(Htsc)_2Cl_2$	287	246	461	448
$Cu(Htsc)_2Br_2$	286	245	455	443
$Ni(Htsc)_2Cl_2$	378	298	523	491
$Ni(Htsc)_2Br_2$	376	295	523	487
$Ni(tsc)_2$	346	326	528	569
$Ni(Htsc)_3Cl_2 \cdot H_2O$	274, 248		400, 376	
$Ni(Htsc)_3Br_2 \cdot H_2O$	271, 245		396, 374	
$Pd(Htsc)_2Cl_2$	305	304	496	500
$Pd(Htsc)_2Br_2$	302	302	496	499
$Pd(Htsc)_2I_2$	297	300		498
$Pd(tsc)_2$	315		499	
$Pt(Htsc)_2Cl_2$	298	340	510	535
$Pt(Htsc)_2Br_2$	292	324	483	510
$Pt(Htsc)_2I_2$	293	334	505	534

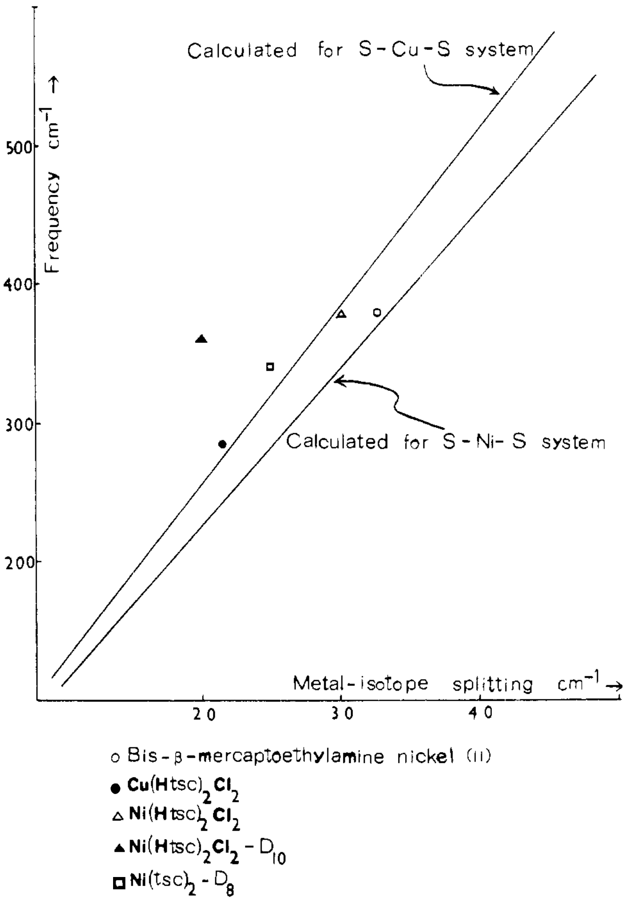


Figure 9. Comparison of the splittings due to the metal-isotope natural abundance with those calculated from a simplified linear "sulfur–metal–sulfur" system.

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(23) Ballard, R. E; Powell, D. B; Jayasooriya, U. A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1111.

the X-ray structural data where the metal ligand bond lengths in the tris complex are about 10% longer than those in the bis complexes.

A summary of the metal–ligand vibrations assigned in this report is given in Table V, which clearly shows a general correlation between the mass of the metal atom and the frequency difference between the symmetric and antisymmetric metal–ligand modes. The frequencies of the antisymmetric modes are higher than the corresponding symmetric modes with Cu(II), almost equal with Pd(II), and lower with Pt(II) complexes.

Conclusions

This investigation illustrates the application of the technique of using the metal-isotope natural abundances,[21] in conjunction with other methods in the assignment of the far-infrared spectra, by providing a means of identifying the nickel–sulfur stretch in $Ni(Htsc)_2Cl_2$, together with an explanation for its exceptionally high deuteration shift and also by confirming the assignment of the metal–sulfur stretching modes in $Cu(Htsc)_2Cl$ and $Ni(tsc)_2$. The higher frequency assigned for the Ni–S stretching mode compares favorably with assignments for similar complexes in the literature.[22,24]

A comparison of the observed metal-isotope natural abundance splittings with that calculated from a highly simplified linear triatomic sulfur–metal–sulfur model is illustrated graphically in Figure 9. The good agreement shown suggests the presence of relatively pure metal-sulfur stretching modes in these complexes except in the case of $Ni(Htsc)_2Cl_2\text{-}d_{10}$, which shows an exceptional deviation arising from vibrational coupling with other modes.

Clearly, this technique of using the metal-isotope natural abundance has its greatest value in cases where the more elegant matrix-isolation technique is inapplicable due to experimental difficulties like insufficient volatility and solubility.

This investigation stresses the need for a reliable assignment before embarking on an approximate normal-coordinate analysis of complex vibrational systems. The relatively new IINS spectroscopy becomes a very powerful tool when used together with the other vibrational spectroscopic techniques in the vibrational analysis of complicated systems. It would be relevant at this point to note the elegance of IINS spectroscopy in the identification of the normal modes involving hydrogen movement in complex systems without depending on the success of deuterium substitution studies with their inherent complications due to the possible changes in the vibrational mode mixing.

Acknowledgment. Assistance given by the University support group headed by D. H. C. Harris at AERE, Harwell, is gratefully acknowledged.

Registry No. $Cu(Htsc)_2Cl_2$, 37981-04-7; $Cu(Htsc)_2Br_2$, 80228-80-4; $Ni(Htsc)_2Cl_2$, 21360-11-2; $Ni(Htsc)_2Br_2$, 53277-11-5; $Ni(tsc)_2$, 21360-12-3; $Ni(Htsc)_3Cl_2$, 36252-57-0; $Pd(Htsc)_2Cl_2$, 21360-15-6; $Pd(Htsc)_2Br_2$, 59532-29-5; $Pd(Htsc)_2I_2$, 59532-30-8; $Pd(tsc)_2$, 21360-16-7; $Pt(Htsc)_2Cl_2$, 21360-18-9; $Pt(Htsc)_2Br_2$, 59598-81-1; $Pt(Htsc)_2I_2$, 59685-11-9; $Ni(Htsc)_3Br_2$, 36252-58-1.

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(24) See, for example: Siiman, O.; Fresco, J. *Inorg. Chem.* **1969**, *8*, 1846. Schlapfer, C. W; Nakamoto, K. *Inorg. Chim. Acta* **1972**, *6(1)*, 177.

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(26) Willis, B. T. M., Ed. "Chemical Applications of Thermal Neutron Scattering"; Oxford University Press: London, 1973.

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Structure and Dynamics of Complexes of the Uranyl Ion with Nonamethylimidodiphosphoramide (NIPA). 2. NMR Studies of Complexes $[UO_2(NIPA)_2X](ClO_4)_2$ with X = H_2O, MeOH, EtOH, or Me_2CO

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The ^{31}P and ^{1}H spectra at −90 °C of the title uranyl complex ions (prepared as solutions of the solid perchlorates in inert anhydrous organic solvents (CH_3NO_2, CH_2Cl_2)) reveal a pentacoordinated arrangement of two symmetrically doubly bonded NIPA molecules and one solvent molecule about the uranyl group. In the case of $[UO_2(NIPA)_2(EtOH)](ClO_4)_2$, an intermolecular exchange between bound and free ethanol molecules is observed above −75 °C upon addition of ethanol to a solution of the complex. The observed rate law, $k_{inter} = kK[EtOH]/(1 + K[EtOH])$ is accounted for by the existence of an outer-sphere complex $[UO_2{}^{2+}(NIPA)_2(EtOH)]EtOH$ in fast equilibrium (K) with the initial complex and free ethanol. The rate-determining step (k) consists of an outer-sphere to inner-sphere interchange of ethanol molecules. The thermodynamic and kinetic parameters are $K(25\ °C) = 15.8\ dm^3\ mol^{-1}$, $k(25\ °C) = 1.0 \times 10^4\ s^{-1}$, ΔH and $\Delta H_{inter}{}^{*} = -4.8$ and 7.6 kcal mol^{-1}, and ΔS and $\Delta S_{inter}{}^{*} = -10.7$ and −14.7 eu. A second exchange takes place at higher temperatures (above −30 °C) yielding full dynamic equivalence of the phosphorus nuclei of the coordinated NIPA molecules. The observed rate law $k_{intra} = k_{ex}/(1 + K[EtOH])$ reveals that the internal rearrangement of NIPA molecules occurs on the complex ion $[UO_2(NIPA)_2(EtOH)]^{2+}$ but not on the outer-sphere complex: $k_{ex}(25\ °C) = 0.91 \times 10^3\ s^{-1}$, $\Delta H_{intra}{}^{*} = 10.6\ kcal\ mol^{-1}$, and $\Delta S_{intra}{}^{*} = -9.4$ eu. Possible mechanisms for this exchange are discussed.

Introduction

In an earlier publication[1] we described the structure of a uranyl complex with the diphosphorylated bidentate ligand nonamethylimidodiphosphoramide (NIPA) = $(NMe_2)_2P(O)NMeP(O)(NMe_2)_2$, a powerful neutral chelating reagent.[2] Standard procedures[3-5] to synthesize NIPA complexes use hydrated metallic perchlorates, which are dissolved in a mixture of ethanol and ethyl orthoformate so as to obtain anhydrous solutions of the metallic perchlorates. The chelating

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