CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

Vibrational Spectra of the Thiocarbonate Complexes of Nickel(II), Palladium(II), and Platinum(II)

BY J. MICHAEL BURKE AND J. P. FACKLER, JR.*

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The infrared and Raman spectra of a series of thiocarbonate transition metal complexes have been measured. The band assignments for the series $M'[M(CS_3)_2]$, M = Ni, Pd, or Pt, were made by observing which bands were relatively unaffected upon variation of the cation M′. These assignments were then extended to $[(Ph_2Me)P]_2M(CS_3)$, $[(Ph_2Me)P]_2M(CS_2O)$, M = Pd or Pt, and $[Ph_3P]_2Pt(CS_2O)$. Band assignments showed that ν(C=S) (1030 cm^{-1}) and ν_{As}(C—S) (850 cm^{-1}) remained constant in the complexes studied, while ν_S(C—S) and ν(M—S) varied in the series $M(CS_3)_2{}^{2-}$, $M(CS_3)$, and $M(CS_2O)$. In this paper we also show that $Ni(CS_3)(NH_3)_3$ and $Pt(CS_3)(NH_3)_2 \cdot H_2O$ reported by Hofmann and reexamined by Krebs are better formulated as $[Ni(NH_3)_6]Ni(CS_3)_2$ and $[Pt(NH_3)_4]Pt(CS_3)_2 \cdot 2H_2O$.

Introduction

Several authors[1] have postulated transition metal thiocarbonate complexes to be formed as unstable intermediates in metal ion analyses. Only recently a series of stable thiocarbonate transition metal complexes have been isolated and characterized.[2,3] As part of a continuing study in our laboratory of *gem*-dithio transition metal complexes, the vibrational spectra of the trithio- and dithiocarbonate complexes of nickel(II), palladium(II), and platinum(II) were investigated.

There have been several vibrational studies of the trithiocarbonate anion.[4] Studies also have been made by Müller and Krebs[5,6] of some complexes reported initially by Hofmann[7-9] which we believe to contain coordinated trithiocarbonate. Müller and Krebs[5,6] were unable to arrive at a definite conclusion regarding the structures of these complexes, due probably to an incorrect assumption regarding their stoichiometry. The isolation[2] and single-crystal X-ray analysis[10] of $[Ph_4As]_2[Ni(CS_3)_2]$ have enabled us to resolve the problem.

The vibrational spectra for a series of compounds $M'[M(CS_3)_2]$, M = Ni, Pd, Pt and M′ = cation, are reported here along with the spectra for a series of bis(phosphine)trithiocarbonatopalladium(II) and -platinum(II) species prepared in our laboratory.

In 1969 the first stable dithiocarbonate transition metal complexes were reported.[3] An alternate preparation has been given by Wilkinson, *et al.*[11] The results of a vibrational study of $[(Ph_2Me)P]_2M(CS_2O)$, M = Pd, Pt, and $[Ph_3P]_2Pt(CS_2O)$ also are reported here and compared with the spectra of the trithiocarbonate complexes.

Experimental Section

The $M(CS_3)_2{}^{2-}$, M = Ni, Pd, Pt, complexes were prepared by the method of Fackler and Coucouvanis[2] and isolated in the solid state in the presence of various cations.

The $[(Ph_2Me)P]_2M(CS_3)$, M = Pd, Pt, and $[Ph_3P]_2M(CS_2O)$, M = Pd, Pt, complexes were prepared by the method of Fackler and Seidel.[3]

The $[Ni(NH_3)_6]Ni(CS_3)_2$ complex was prepared by the method of Müller and Krebs,[6] while $[Pt(NH_3)_4]Pt(CS_3)_2 \cdot 2H_2O$ was prepared by the method of Hofmann.[7] Conductivity measurements were determined on a Leeds and Northrup Model 4866 bridge using a cell calibrated with 0.020 *M* KCl solution. The magnetic susceptibility of $[Ni(NH_3)_6]Ni(CS_3)_2$ was determined by the Gouy method with $HgCo(SCN)_4$ and $Ni(en)_3S_2O_3$ as calibrants.[12] The ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14R recording spectrophotometer.

Infrared spectra were obtained from 200 to 4000 cm^{-1} by using a Beckman IR-12 diffraction grating double beam recording spectrophotometer. Calibration of the frequency was made with water vapor, methane, and CO_2. Spectra of the compounds were obtained in cesium iodide, cesium bromide, and potassium bromide pellets as well as in Nujol mulls supported on cesium bromide plates.

Raman spectra were obtained by using a Cary 81 He–Ne laser Raman spectrophotometer. Raman spectra could be obtained only for the palladium(II) and platinum(II) species, as the nickel(II) compounds proved to be too highly colored.

Results

Due to the fact that the anionic trithiocarbonate complexes could be isolated only in the presence of large cations, the spectrum of the anion with several different cations had to be obtained in order to facilitate the assignments. Recorder traces of representative spectra of the bis(trithiocarbonato)metal complexes are presented in Figure 1, while a listing of the bands of all the complexes studied is given in Tables I and II. (Due to reproduction difficulties, the wavelength scale on the figures is not accurate over the entire spectral range.)

Recorder traces of some representative vibrational spectra of $L_2M(CS_3)$, $L_2M(CS_2O)$ (M = Pd(II), Pt(II); L = $(Ph_2Me)P$), and $Pt(CS_2O)Ph_3P$ are presented in Figures 2 and 3, while Tables III and IV list the bands corresponding to $M(CS_3)$ and $M(CS_2O)$.

The vibrational spectral bands of $[Ni(NH_3)_6]Ni(CS_3)_2$ and $[Pt(NH_3)_4]Pt(CS_3)_2 \cdot 2H_2O$ are listed in

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[1] D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970), and references therein.

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

[3] J. P. Fackler, Jr., and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).

[4] B. Krebs, A. Müller, and G. Gattow, *Z. Naturforsch. B*, **20**, 1017 (1965); *Z. Anorg. Allg. Chem.*, **337**, 279 (1965); H. Seidel, *Naturwissenschaften*, **52**, 257 (1965); A. Müller and M. Stockburger, *Z. Naturforsch. A*, **20**, 1242 (1965); B. Krebs and A. Müller, *Spectrochim. Acta*, **22**, 1532, 1535 (1966); *Z. Naturforsch. A*, **20**, 1124 (1965); G. Nagarajan and N. Müller, *Z. Naturforsch. B*, **21**, 393 (1966); A. Fadini, A. Müller, and B. Krebs, *Z. Naturforsch. A*, **20**, 1241 (1965).

[5] A. Müller and B. Krebs, *Z. Anorg. Allg. Chem.*, **345**, 165 (1966).

[6] B. Krebs and A. Müller, *Z. Naturforsch. A*, **20**, 1664 (1965).

[7] K. A. Hofmann, *Z. Anorg. Chem.*, **14**, 263 (1897).

[8] K. A. Hofmann and F. Hochtlen, *Ber.*, **36**, 1146 (1903).

[9] O. F. Wiede and K. A. Hofmann, *Z. Anorg. Chem.*, **11**, 379 (1896).

[10] J. S. McKechnie, S. L. Miesel, and I. C. Paul, *Chem. Commun.*, 152 (1967).

[11] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

[12] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 415.

TABLE I

INFRARED SPECTRAL BANDS OF $M(CS_3)_2^{2-}$ (M = Ni, Pd, Pt)[a]

Cation	Metal	C–S str (exocyclic) (B_{3u})	C–S asym str (endocyclic) (B_{2u})	C–S sym str (endocyclic) (B_{3u})	M–S sym str (B_{3u})	M–S asym str (B_{2u})
Ph_4As^+	Ni(II)	1014 (vs)[c]	843, 849 (db, s)[c]	488 (w, sh)[c]	383 (m)	
$[(CH_3)_4N]^+$	Ni(II)	1015 (vs)	855 (m)	489 (w)	385 (m)	
$[(C_2H_5)_4N]^+$	Ni(II)	1038 (vs)[c]	851 (m)[c]	483 (w)	387 (m)	
$[(C_3H_7)_4N]^+$	Ni(II)	1029 (vs)	847 (m), 842 (m)[c]	487 (w)	386 (m)	367 (vw, sh)
$[(C_4H_9)_4P]^+$	Ni(II)	1029 (vs)	853 (m)	485 (w)	385 (m)	
$[(Ph_3Bz)P]^+$[b]	Ni(II)	1029 (vs)	858 (vs)	*c*	385 (m)	367 (vw)
Cs^+	Ni(II)	1015 (vs), 1026 (sh)	856 (m)	479 (w)	383 (m)	367 (vw)
Ph_4As^+	Pd(II)	1018 (vs)[c]	840 (m)	489 (w, sh)	339 (s)[c]	290 (m)
$[(C_3H_7)_4N]^+$	Pd(II)	1025 (s, br)	843, 836 (db, m)	483 (vw)	344 (m)	280 (w)
$[(C_4H_9)_4P]^+$	Pd(II)	1024 (s)	848 (w)	484 (vw)	343 (m)	290 (w)
$[(Ph_3Bz)P]^+$[b]	Pd(II)	1021 (vs)	846 (s)	488 (w)[c]	343 (m)	290 (m)
Ph_4As^+	Pt(II)	1032 (vs)[c]	837, 832 (db, m)	478 (m)[c]	350 (m)[c]	272 (m)
$[(C_3H_7)_4N]^+$	Pt(II)	1037 (s, br)	833, 825 (db, m)	481 (vw)	360, 351 (db, vw)	278 (m)
$[(C_4H_9)_4P]^+$	Pt(II)	1029 (s)	833 (m)	475 (w)	358 (vw, br)	277 (m)
$[(Ph_3Bz)P]^+$[b]	Pt(II)	1031 (s)	831 (vw)	*c*	324 (w)?	280 (w)
Cs^+	Pt(II)	1030 (vs)	863, 840 (db, m)	481 (w)	356 (m) 377 (w)	275 (s)

[a] All values are in cm^{-1}. Key: s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, db = doublet. [b] Ph_3Bz = triphenylbenzyl. [c] Cation bands interfere with these bands.

TABLE II

RAMAN SPECTRAL BANDS OF $M(CS_3)_2^{2-}$ (M = Pd, Pt)[a]

Cation	Metal	C–S str (exocyclic) (A_g)	C–S asym str (endocyclic) (B_{1g})	C–S sym str (endocyclic) (A_g)	M–S sym str (A_g)	M–S asym str (B_{1g})	Ring def (B_{1g})	Ring def (A_g)
Ph_4As^+	Pd(II)	1028 (s)[b]	840 (vw)	509 (m)	375 (w, br)	321 (m)	240 (m)	185 (s)
$[(Ph_3Bz)P]^+$	Pd(II)	1026 (s)		506 (m)	377 (w, br)	322 (m)		
Ph_4As^+	Pt(II)	1026 (w)[b]		517 (w)	403 (m)	339 (w)		
$[(C_3H_7)_4N]^+$	Pt(II)	1038 (vw)		510 (m)	400 (m)	339 (m)		
$[(C_4H_9)_4P]^+$	Pt(II)	1035 (w)		511 (m)	402 (s)	335 (m)		
Cs^+	Pt(II)	1055 (w)?		513 (m)	398 (m)	336 (w)		211 (w)

[a] All bands are in Δ cm^{-1}. [b] Partially obscured by cation bands.

TABLE III

INFRARED AND RAMAN SPECTRAL BANDS OF $L_2M(CS_3)$ (M = Pd, Pt; L = $(Ph_2Me)P$)[a]

Metal	Type	C–S str A_1	C–S asym str B_2	C–S sym str A_1	M–S sym str A_1	M–S asym str B_2	Ring def A_1
Pd(II)	Ir	1050 (s)	858 (w), 839 (vw)	511 (m)	371 (w)	337 (vw)	270 (vw)
	R	1046 (s)		510 (w)	370 (s)	338 (vw)	274 (m)
Pt(II)	Ir	1053 (s)	856 (vw), 837 (vw)	515 (s)	390 (vw)	343 (vw)	254 (vw)
	R	1056 (vs)		513 (m)	390 (vw)	344 (vw)	254 (vw)

[a] All infrared values are in cm^{-1} while the Raman values are in Δ cm^{-1}.

TABLE IV

INFRARED AND RAMAN SPECTRAL BANDS OF $L_2M(CS_2O)$ (M = Pd, Pt; L = $(Ph_2Me)P$, Ph_3P)[a]

L	Metal	Type	C–O[b] str A_1	C–S asym str B_2	C–S sym str A_1	M–S sym str A_1	M–S asym str B_2	Ring def A_1
$(Ph_2Me)P$	Pd(II)	Ir	1681 (s) 1603 (vs)	834 (m)	562 (vw)	388 (w)	312 (vw)	287 (vw)
		R	1606 (vw)		562 (w)	388 (s)	310 (m)	286 (s)
$(Ph_2Me)P$	Pt(II)	Ir	1696 (s) 1681 (sh) 1615 (s)	836 (m)	555 (vw)	409 (vw)	311 (vw)	270 (w)
		R	1618 (vw)		562 (w)	410 (m)	307 (m)	270 (s)
Ph_3P		Ir	1701 (s) 1624 (vs)	845 (m)	562 (w)	405 (vw)		271 (w)
		R	1618 (vw)		562 (w)	406 (w)	306 (w)	266 (vw)

[a] All infrared bands are in cm^{-1} while the Raman bands are in Δ cm^{-1}. [b] A combination band is also in this column. See text for explanation.

Tables V and VI, together with the spectra reported by Müller and Krebs[6] for $Ni(CS_3)(NH_3)_3$. The uv–visible spectral bands of the nickel complex are presented in Table VII, together with those reported in the literature for analogous compounds. Both complexes are 1:1 electrolytes in *N,N*-dimethylformamide with Λ (10^{-3} *M*) = 98 ohm^{-1} cm^{-1} (25°) for the nickel complex.

The gram magnetic susceptibility, χ_g, for $[Ni(NH_3)_6]Ni(CS_3)_2$ is 10.20×10^{-6} cgsu, making $\chi_M = 4447 \times 10^{-6}$ cgsu at 21°. Correcting for diamagnetism[12] gives $\chi_M^{cor} = 4661 \times 10^{-6}$ cgsu. Thus the magnetic

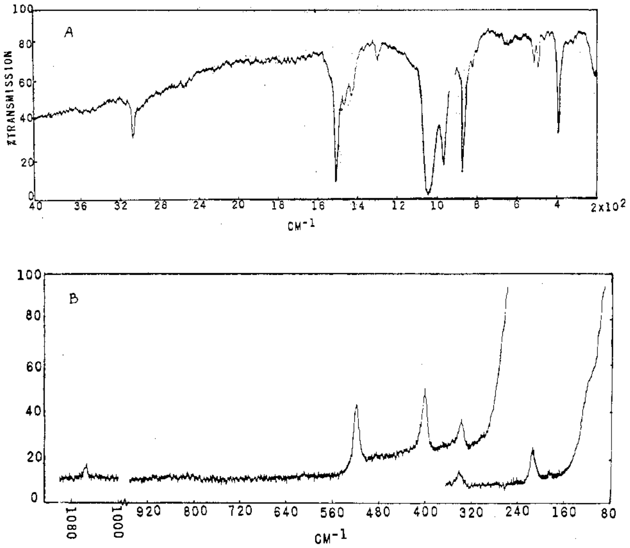


Figure 1.—Schematic reproductions of the vibrational spectra of some $M(CS_3)_2^{2-}$ species: A, infrared spectrum of $[(CH_3)_4N]_2Ni(CS_3)_2$; B, Raman spectrum of $Cs_2Pt(CS_3)_2$.

TABLE V

INFRARED SPECTRAL BANDS OF THE NICKEL COMPLEX, $Ni(CS_3)_2^{2-}$, AND $Ni(NH_3)_6^{2+}$

Complex		$Ni(CS_3)_2^{2-}$	$Ni(NH_3)_6(ClO_4)_2$	
This work	Ref 6	This work	Ref 18	Assignment
3313 (m)	3300 (m)		3397, 3312	$\nu_s(NH)$, sym str
1605 (m)	1612 (m)		1618	$\delta_e(NH_3)$, def
1252 (w)	1252 (w)		1236	$\delta_s(NH_3)$, sym NH_3 def
1223 (m)	1225 (m)			
1000 (s)	1000 (s)	1015 (vs)		C–S str (exocyclic)
857 (m)	860 (m)	855 (m)		C–S asym str (endocyclic)
641 (m)	635 (m)		(620)	$\rho_r(NH_3)$, NH_3 rock
507 (w)	505 (m)	508 (vw)		C–S sym str (R active) or H_2O
492 (w)	490 (m)	488 (w)		C–S sym str (endocyclic)
388 (s)	386 (s)	383 (m)		Ni–S sym str
369 (vw)	366 (w)?	367 (vw)		Ni–S asym str
321 (vw)?	328 (m)		334 (s)[a]	Ni–N str

[a] L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3,** 1772 (1964) (from $Ni(NH_3)_6Cl_2$).

TABLE VI

INFRARED SPECTRAL BANDS OF THE PLATINUM COMPLEX, $Pt(CS_3)_2^{2-}$, AND $Pt(NH_3)_4Cl_2$

Complex	$Pt(CS_3)_2^{2-}$	$Pt(NH_3)_4Cl_2$ (ref 18)	Assignment
3262 (m)			H_2O
1608 (m)		1563	$\delta_d(NH_3)$
1331 (w)		1325	$\delta_s(NH_3)$
1306 (s)			
1005 (s)	1030 (vs)		C–S str (exocyclic)
864 (m)		842	$\rho_r(NH_3)$
827 (m)	830 (m)		C–S asym str (endocyclic)
		510	M–N str
	505 (w)		C–S sym str (R active) or H_2O
492 (vw)	481 (vw)		C–S sym str (endocyclic)
390 (vw)	360 (vw)		Pt–S sym str
274 (m)	277 (m)		Pt–S asym str or δ_{NMN}
245 (m)		297	δ_{NMN} or Pt–S asym str

moment $\mu_{eff}^{cor}(294°K)$ for $[Ni(NH_3)_6]Ni(CS_3)_2$ is 3.32 BM.

TABLE VII

ELECTRONIC SPECTRAL BANDS OF THE NICKEL COMPLEX, $Ni(CS_3)_2^{2-}$, AND $Ni(NH_3)_6^{2+}$

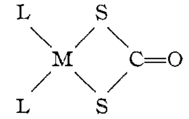
Complex (in DMF)		$Ni(CS_3)_2^{2-}$ (ref 2)[a] (in acetonitrile)		$Ni(NH_3)_6Cl_2$ (ref *b*) (in water)	
ν_{max}, Å	ϵ, l. mol^{-1} cm^{-1}	ν_{max}, Å	ϵ, l. mol^{-1} cm^{-1}	ν_{max}, Å	ϵ, l. mol^{-1} cm^{-1}
9300	14			9302	4
7600	25			7605	
3600	1.8×10^4			3600	
6100	270	6100 (sh)	150		
5450	1900	5435	(1200)		
5050	1×10^4	5050	10^3		
4800	4.3×10^3	4600 (sh)	4.4×10^3		
3330	3.4×10^4	3300	(4.3×10^4)		
2800	2.0×10^4	2800	2.7×10^4		
2600	1.4×10^4	2600	1.94×10^4		

[a] The extinction coefficients of $Ni(CS_3)_2^{2-}$ reported in ref 2 are too low by a factor of 10. The values reported here have been adjusted accordingly. [b] K. Jorgensen, *Acta Chem. Scand.*, **9,** 1362 (1955).

Discussion

The vibrational bands belonging to the trithiocarbonate portion of $M'[M(CS_3)_2]$ complexes were deduced by observing which bands remained relatively unchanged when the cation M′ was varied. These results were used to make the assignments for the $L_2M(CS_3)$ and $L_2M(CS_2O)$ species. A D_{2h} symmetry was assumed for $M(CS_3)_2^{2-}$ (see Figure 4) while a C_{2v} symmetry was assumed for $L_2M(CS_3)$ and $L_2M(CS_2O)$.

Carbon–Oxygen and Carbon–Sulfur Double Bond Stretching Vibrations.—A comparison of the spectra of $L_2M(CS_2O)$ with that of $L_2M(CS_3)$ (see Figures 2 and 3, Tables III and IV) clearly shows the presence of two bands between 1600 and 1700 cm⁻¹ in $L_2M(CS_2O)$ which are not present in $L_2M(CS_3)$. This would suggest that these two bands are due to a C=O stretching vibration[13] as implied by the proposed[3] structure, I. The



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appearance of two bands in this region has also been observed by Wilkinson, *et al.*,[11] in similar compounds. We attribute the lower and more intense frequency to the ν(C=O) while the less intense higher energy band is thought to be due to Fermi resonance between the carbon–oxygen stretching mode (A_1) and the first overtone band of the carbon–sulfur asymmetric stretching mode ($B_2 \times B_2 = A_1$). This C=O stretching frequency is very near the position that was observed by Nakamoto[13] for the C=O stretch in $[Co(NH_3)_4(CO_3)]^+$.

A strong band is observed around 1025 cm⁻¹ in all of the trithiocarbonate complexes but is absent in $L_2M(CS_2O)$ and can easily be attributed to the carbon–sulfur exocyclic stretching mode. The frequency of the C=S band in the $L_2M(CS_3)$ species is increased by about 25 cm⁻¹ and sharpened considerably compared to the same band in $M(CS_3)_2^{2-}$. Removal of the cation–anion interactions could very well account for these phenomena. The position of the C=S stretching vibration is somewhat lower than the 1050–1200 cm⁻¹ range[14] normally associated with carbon–sulfur double

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(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 170.

(14) L. T. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1956, p 356.

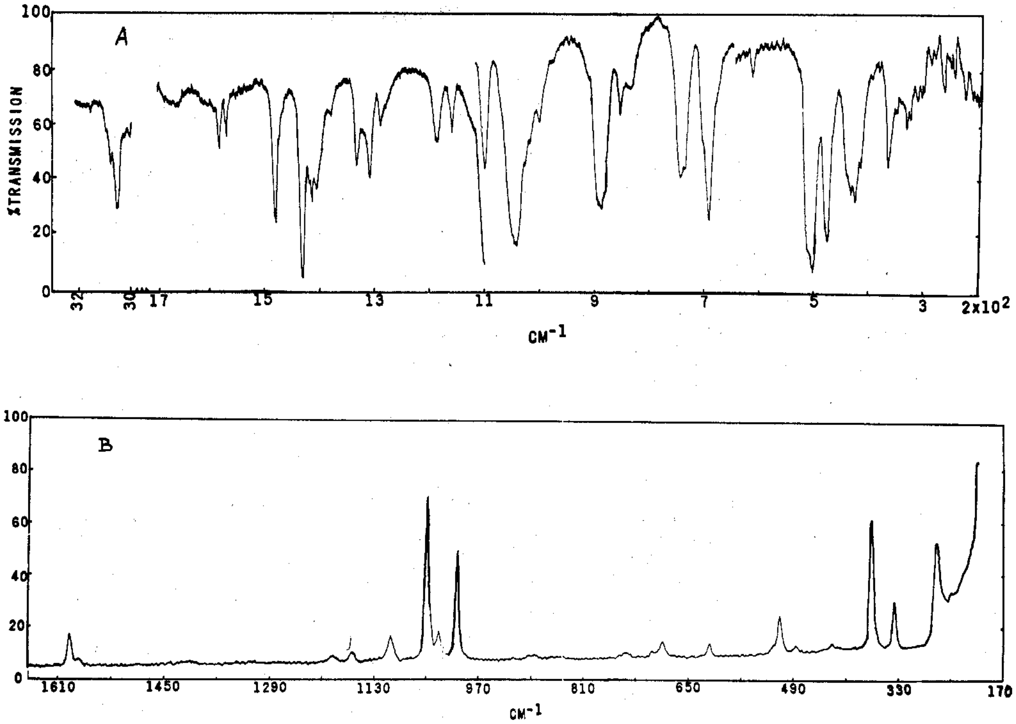

Figure 2.—Schematic reproductions of the vibrational spectra of some $L_2M(CS_3)$ species: A, infrared spectrum of $[(Ph_2Me)P]_2Pd(CS_3)$ (CsBr pellet); B, Raman spectrum of $[(Ph_2Me)P]_2Pd(CS_3)$.

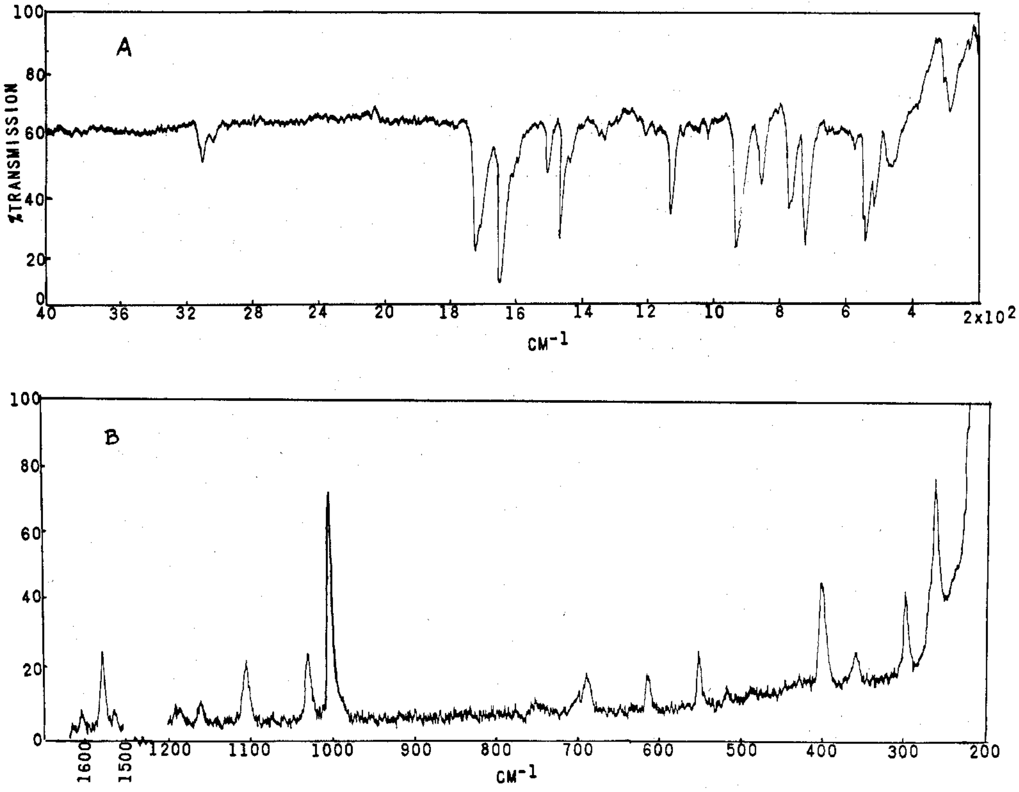

Figure 3.—Schematic reproductions of the vibrational spectra of some $L_2M(CS_2O)$ species: A, infrared spectrum of $[(Ph_2Me)P]_2Pt(CS_2O)$ (CsBr pellet); B, Raman spectrum of $[(Ph_2Me)P]_2Pt(CS_2O)$.

bond vibrations. It is, however, near the carbon–sulfur stretching band of the xanthates.[15]

Carbon–Sulfur Single Bond Stretching Vibrations.—Symmetry predicts two carbon–sulfur endocyclic stretching vibrations for $M(CS_3)$ and $M(CS_2O)$ and two infrared active plus two Raman active carbon–sulfur endocyclic stretching vibrations for $M(CS_3)_2{}^{2-}$.

In most complexes studied here, the higher frequency carbon–sulfur stretching mode appears as a distinct

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[15] (a) U. Agarwala, Lakshmi, and P. B. Rao, *Inorg. Chim. Acta*, **2**, 337 (1968); (b) G. W. Watt and B. J. McCormick, *Spectrochim. Acta*, **21**, 753 (1965); (c) L. H. Little, G. W. Poling, and J. Leja, *Can. J. Chem.*, **39**, 745, 1783 (1961); (d) M. L. Shankaranarayana and C. C. Patel, *Can. J. Chem.*, **39**, 1633 (1961).

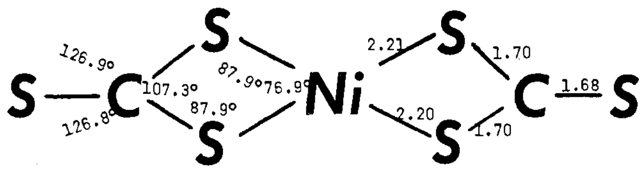


Figure 4.—Bond lengths and angles in the bis(trithiocarbonato)-nickel(II) anion.[10]

weak band between 825 and 850 cm^{-1}. However, it is obscured by other bands in some of the cases. There is little or no shift of this band on going from $M(CS_3)_2^{2-}$ to $L_2M(CS_3)$ to $L_2M(CS_2O)$.

The lower frequency carbon–sulfur stretching vibrations (near 500 cm^{-1}) occur in different positions in the Raman spectra of $M(CS_3)_2^{2-}$ from their positions in the infrared. This lack of coincidence of the Raman and infrared bands in $M(CS_3)_2^{2-}$ may be indicative of solid state interactions or it may be a result of ligand–ligand interactions. A shift to higher frequencies is noted on going from $M(CS_3)_2^{2-}$ to $M(CS_3)$ to $M(CS_2O)$. Since there is probably some mixing of these low-frequency modes, it is very difficult to say unequivocably that the shift of ν(C–S) to higher energies on going from $M(CS_3)_2^{2-}$ to $L_2M(CS_3)$ to $L_2M(CS_2O)$ is indicative of a general strengthening of the C–S bond, although the idea is not unrealistic.

Metal–Sulfur Stretching Vibrations.—Four metal–sulfur stretching vibrations are expected for $M(CS_3)_2^{2-}$ and two for $L_2M(CS_3)$ and $L_2M(CS_2O)$. The two infrared active metal–sulfur stretching vibrations for $M(CS_3)_2^{2-}$ are assigned the frequencies 385 and 365 cm^{-1} for nickel, 343 and 288 cm^{-1} for palladium, and 340 and 276 cm^{-1} for platinum, while the two Raman active vibrations are assigned at 376 and 321 cm^{-1} for palladium and 400 and 338 cm^{-1} for platinum. The noncoincidence of the infrared and Raman active vibrational frequencies could be indicative of interligand interaction.

There exists an increase of 25 cm^{-1} in ν(M–S) on going from $M(CS_3)_2^{2-}$ to $M(CS_3)$ to $M(CS_2O)$ (see Tables I to IV). This shifting correlates with a general strengthening of the metal–sulfur bond; however, one must be wary of any frequency–force constant relations in this region due to the large amount of mixing of vibrational modes, especially in these ring compounds.

Ring Vibrations.—Several other vibrational bands are expected for these dithiocarbonate complexes. The assignment of these bands in the $M'[M(CS_3)_2]$ complexes was made by observing which bands remained relatively unchanged when M′ was varied. In the case of $L_2M(CS_3)$ and $L_2M(CS_2O)$, the phosphine ligand bands were assigned by reference to spectra of similar compounds[16,17] and the bands remaining were assumed to be due to $M(CS_3)$ or $M(CS_2O)$.

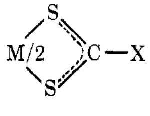
There are 21 normal vibrations (15 in-plane and 6 out-of-plane) for $M(CS_3)_2^{2-}$ and 9 each (7 in-plane and 2 out-of-plane) for $M(CS_3)$ and $M(CS_2O)$. Only 12 bands for $M(CS_3)_2^{2-}$ and 6 bands for $M(CS_3)$ and $M(CS_2O)$ could be assigned with any certainty, while the remaining bands are thought to be either very weak or below 200 cm^{-1}.

The Amine Trithiocarbonate Complexes.—As mentioned in the Introduction, an interesting series of amine trithiocarbonate metal complexes was prepared by Hofmann, *et al.*,[7-9] at the turn of the century. Our studies of the $Ni(NH_3)_3(CS_3)$ and $Pt(NH_3)_2(CS_3)\cdot H_2O$ complexes (summarized in Tables V to VII) show that these complexes are better formulated as $[Ni(NH_3)_6]Ni(CS_3)_2$ and $[Pt(NH_3)_4]Pt(CS_3)_2\cdot 2H_2O$.

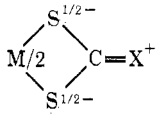
The reported[6] infrared spectrum of $Ni(NH_3)_3(CS_3)$ (which we have reexamined) can be explained very easily as arising from overlapping spectra of $Ni(CS_3)_2^{2-}$ and $Ni(NH_3)_6^{2+}$. The anion greatly affects the $Ni(NH_3)_6^{2+}$ spectrum but the infrared spectrum[18] of the $[Ni(NH_3)_6](ClO_4)_2$ species agrees very well with that of the complex reported here. The slight shifting of certain bands associated with the $Ni(CS_3)_2^{2-}$ species is probably due to hydrogen bonding.[18] The electronic spectrum of $[Ni(NH_3)_6]Ni(CS_3)_2$ (Table VII) clearly shows the presence of $Ni(CS_3)_2^{2-}$ which obscures almost any other bands; however, the low-energy ligand-field bands can be assigned to $Ni(NH_3)_6^{2+}$. These spectral data, together with the conductivity and magnetic data, substantiate a $[Ni(NH_3)_6]Ni(CS_3)_2$ structure for the nickel complex prepared by Hofmann.[9]

Only the infrared spectrum of the $Pt(NH_3)_2(CS_3)\cdot H_2O$ complex was studied, but the spectrum can be compared quite readily to overlapping spectra of $Pt(CS_3)_2^{2-}$ and $Pt(NH_3)_4Cl_2$.[18] There are some discrepancies in the bands but they can be explained by varying amounts of hydrogen bonding in the complex. These data suggest that Hofmann's[7] complex is $[Pt(NH_3)_4]Pt(CS_3)_2\cdot 2H_2O$.

Conclusions on Bonding.—The higher frequency carbon–sulfur endocyclic stretching frequency is generally reported as the "carbon–sulfur stretching frequency" in the infrared studies of metal–sulfur chelate compounds. It is interesting to note that there is a substantial frequency spread (~200 cm^{-1}) for this mode in a variety of 1,1-dithio complexes. The position of this band may indicate the relative strength of the C–S bond in these complexes. This band appears at 1025 cm^{-1} in xanthate complexes,[15] between 910 and 950 cm^{-1} in the 1,1-disubstituted-2,2-dithioethylene complexes,[19] at 850 cm^{-1} in the compounds studied here, and at 820 cm^{-1} in $Pt(S_2CNH_2)_2$.[20] These bands are higher than the 600–700 cm^{-1} range of the carbon–sulfur single bond stretching frequency, but below the range of the carbon–sulfur double bond stretching frequency.[14] The results are consistent with a predominant resonance structure for xanthates (where X = OR),[15] given by II, and for thiocarbonates (X = S or O) and $Pt(S_2CNH_2)$,[20] III. The ethylenedithiolate complexes[19] are expected to exhibit a structure intermediate between II and III.



II



III

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[16] D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967.

[17] Reference 13, p 205.

[18] Reference 13, p 150.

[19] K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, **24**, 1092 (1970); K. A. Jensen and L. Henriksen, *ibid.*, **24**, 3213 (1970). See also ref 2.

[20] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).

The calculated carbon–sulfur stretching force constants are consistent with the above structures with F_{C-S} in bis(ethyl xanthato)nickel(II)[15a] equal to 3.7 mdyn/Å and in bis(dithiocarbamato)platinum(II)[20] equal to 3.00 mdyn/Å. [See also the calculations for bis(*N*,*N*-dimethyldithiocarbamato)nickel(II)[21] and the questions raised about this work by Jensen and Krishnan.[22]] These force constants are slightly larger than that of the pure carbon–sulfur single bond (2.50 mdyn/Å for diethyl thioether)[20] and smaller than that of the pure C–S double bond (7.8 mdyn/Å for CS_2).[23]

In an attempt to obtain an estimate of the strength of the metal–sulfur bonds in $M(CS_3)_2^{2-}$, a complete normal-coordinate analysis treatment was initiated. Preliminary calculations showed the existence of considerable mixing of modes in the low-frequency region. From the results of normal-coordinate analyses of similar compounds,[15a,20,21,24] vibrational mixing of this type is recognized to be common. As a result a direct correlation of the metal–sulfur stretching frequencies with the metal–sulfur bond strengths cannot be made. Previous normal-coordinate analyses of metal–sulfur chelate compounds have not considered interligand interactions.[25]

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[21] G. Durgaprasad, D. N. Sathyamarayana, and C. C. Patel, *Can. J. Chem.*, **47**, 631 (1969).

[22] K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, **24**, 1088 (1970).

[23] L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

[24] J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Jap.*, **37**, 528 (1964); A. Finch, R. C. Poller, and D. Steel, *Trans. Faraday Soc.*, **61**, 2628 (1965); Lakshmi, P. B. Rao, and U. Agarwala, *Appl. Spectrosc.*, **25**, 207 (1971).

[25] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 331 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO, LONDON, ONTARIO, CANADA

Cationic Organometallic Complexes with Unsaturated Systems. IV. Dimethylplatinum(IV) Cations. Chemical Reactivity and a Nuclear Magnetic Resonance Trans-Influence Series

BY H. C. CLARK* AND L. E. MANZER

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Complexes of the type $[Pt(CH_3)_2Q_2L_2]^{2+}$ and $[Pt(CH_3)_2Q_2LI]^{+}$ have been prepared, where Q = $P(CH_3)_2(C_6H_5)$ and L is a ligand such as a phosphite, nitrile, isocyanide, phosphine, etc. $^{2}J(Pt(IV)-CH_3)$ is used to establish an nmr trans-influence series and the ratio of this coupling constant with $^{2}J(Pt(II)-CH_3)$ for an analogous series of complexes is discussed. The N≡C stretching frequencies for a series of cationic ethyl isocyanide complexes are discussed in terms of the electron density on platinum. The reactions of the dimethylplatinum(IV) cations with 1-butyn-4-ol and pentafluorobenzonitrile are compared with those of the corresponding methylplatinum(II) compounds.

Introduction

Trimethylplatinum(IV) iodide was the first organoplatinum complex to be prepared,[1] and most of the chemistry of organoplatinum(IV) has evolved from this compound.[2] Dimethylplatinum(IV) complexes have received much less attention due to their difficulty of preparation rather than to any inherent instability.[3]

While investigating the nature of the Pt–CF_3 bond in a series of CF_3–Pt(II) and CF_3–Pt(IV) complexes[4] we discovered that the iodide trans to CF_3 was quite labile to the extent that we were able to prepare several platinum(IV) cations including a carbene complex.[5] Consequently, the apparent stability of these platinum(IV) cations prompted us to extend our investigations to the synthesis of other organoplatinum(IV) cations.

We have recently been interested in the reactivity of unsaturated systems with methylplatinum(II) cations[6–10] so it was also of interest to examine the reactivity of these ligands when present in organoplatinum(IV) cations. On oxidation from Pt(II) to Pt(IV), two electrons are removed from the metal resulting in a contraction of the metal orbitals and it is these orbitals that are used for π back-donation into ligand π^* orbitals. Therefore, any complexes with unsaturated ligands, that rely on M $(d\pi) \rightarrow$ L (π^*) bonding would be expected to be less stable for Pt(IV) compared with Pt(II).

In this paper we report the synthesis of a wide variety of dimethylplatinum(IV) cations and the reactions of these cations with acetylenes and pentafluorobenzonitrile. We also discuss the relationship between $^{2}J(^{195}Pt-CH_3)$ and the nmr trans influence of a neutral ligand trans to the methyl group in such dimethylplatinum(IV) cations.

Results and Discussion

I. Preparation of the Complexes.—One or both of the iodine atoms in dimethylbis(dimethylphenylphos-

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[1] W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, 95 (1909).

[2] For a recent review of organoplatinum(IV) compounds see J. S. Thayer, *Organometal. Chem. Rev., Sect. A*, **5**, 53 (1970).

[3] J. R. Hall and G. A. Swile, *Aust. J. Chem.*, **24**, 423 (1971).

[4] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1786 (1972).

[5] M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 1485 (1971).

[6] H. C. Clark and L. E. Manzer, *ibid.*, 387 (1971).

[7] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971).

[8] M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 2557 (1971).

[9] H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, **30**, C89 (1971).

[10] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 503 (1972).

[11] H. C. Clark and J. D. Ruddick, *ibid.*, **9**, 1226 (1970).