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Vibrational Spectra of Dithioaryl Acid Complexes of Nickel(II), Palladium(II), Platinum(II), and Zinc(II), and Their Sulfur Addition Products. The X-Ray Crystal Structure of the Dimer of Bis(dithiocumato)platinum(II)—A Material with a 2.87-Å Metal–Metal Bond

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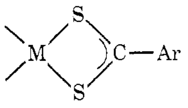
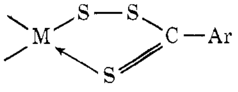
Infrared spectra have been obtained from 200 to 4000 cm^{-1} for several dithio- and perthiobenzoate, -toluate, and -cumate complexes of nickel(II), palladium(II), platinum(II), and zinc(II) and the mixed ligand species of the nickel triad metals. Raman spectra have been obtained for the zinc complexes. Assignments are made for the ligand vibrations and the metal–sulfur stretches. These latter bands appear below 400 cm^{-1}. Of particular interest is the carbon–sulfur stretching region, 900–1100 cm^{-1}, where four bands are observed in the mixed ligand dithio–perthio species. Two bands separated by only 50 cm^{-1} are observed in the bis(dithioarylato)metal complexes, and two bands separated by 125 cm^{-1} are found in the bis(perthioarylato)metal species. By assigning the four bands between 900 and 1100 cm^{-1} to the carbon–sulfur stretching frequencies in the bis(dithioarylato)platinum(II) complexes, the conclusion is reached that all of the bis(dithioarylato)platinum(II) complexes studied here have a structure similar to that observed crystallographically for bis-μ-dithiocumato-bis-(dithiocumato)diplatinum(II), $Pt_2(p\text{-dtc})_4$. This material forms triclinic crystals, a = 15.564 (6), b = 15.480 (6), c = 12.555 (3) Å; α = 90.58 (1), β = 116.80 (1), γ = 122.55 (1)°; and Z = 2. Full-matrix least-squares refinement on 3459 nonzero reflections obtained diffractometrically in the copper Kα sphere produced a converged solution with R_1 = 9.9 and R_2 = 12.5. The dithiolate dimer shows a platinum–platinum distance of 2.870 (2) Å in a distorted square antiprism of sulfur atoms. There are two bridging and two terminal dithiolate ligands accounting for the observed multiplicity of ligand bands in the vibration spectrum.

Introduction

Dithiocarboxylic acids have been known for some time and the preparation of their metal complexes, I,



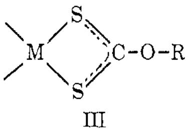
I



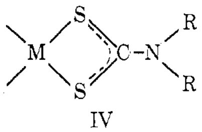
II

has been reviewed by Coucouvanis[1] and by Fetchin.[2] Vibrational spectra of these complexes have not been described in detail to date. Certain dithiocarboxylate complexes are known to undergo oxidative addition of sulfur[1-3] to form complexes containing the perthiocarboxylate[4] ligand, II.

In this paper we report the results of an investigation of the vibrational spectra of several nickel(II), palladium(II), platinum(II), and zinc(II) complexes of dithio- and perthioaryl acids. There are features strikingly different from existing vibrational data for other *gem*-dithio transition metal complexes, such as the xanthates, III, or dithiocarbamates, IV. To date



III



IV

stable neutral perthio complexes have not been obtained with xanthates or dithiocarbamates.

A detailed description of the molecular structure of $Pt_2(p\text{-dtc})_4$ is presented here along with a description of the vibrational spectra and bonding in this and related dimeric platinum(II) complexes. A preliminary report of the structure of $Pt_2(p\text{-dtc})_4$ has been published earlier.[5]

Experimental Section

The compounds $M(dtb)_2$ and $M(p\text{-dtc})_2$ (M = Ni, Pd, Zn) as well as $Pd(p\text{-dtt})_2$ and $Zn(p\text{-dtt})_2$ were used as obtained[6] without further purification. $Ni(p\text{-dtt})_2$ was prepared as published.[3] $[Pt(p\text{-dtt})_2]_2$ and $[Pt(p\text{-dtc})_2]_2$ were also obtained[2] and used without further purification. $[Pt(dtb)_2]_2$ was prepared from $Zn(dtb)_2$ in a manner analogous to that used[2b] to prepare $[Pt(p\text{-dtt})_2]_2$. Low solubility precluded the accurate measurement of the molecular weights of these platinum complexes.

Sulfur-rich dithiolates $Zn(dtbS)_2$, $Zn(p\text{-dttS})_2$, $Ni(p\text{-dttS})_2$, $Ni(p\text{-dtcS})(p\text{-dtc})$, $Pd(p\text{-dtcS})(p\text{-dtc})$, $Zn(p\text{-dtcS})_2$, and $Ni(p\text{-dtcS})_2$ were obtained[6] and used without further purification.

Infrared spectra were obtained from 200 to 4000 cm^{-1} with a Beckman IR-12 diffraction grating double beam recording spectrophotometer. Calibration of the frequency was made with water, 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 zinc species as the other compounds proved to be too highly colored. Spectral data are presented in Tables I and II.

X-Ray Crystallographic Structural Data

Opaque crystals of $[Pt(p\text{-dtc})_2]_2$ as obtained from $CHCl_3$ were examined optically. A crystal suitable for diffraction was mounted on a glass fiber and precession and Weissenberg photographs (1st, 2nd, and 3rd levels) with molybdenum and copper radiation, respectively, were taken. These data suggested a triclinic cell with $V \approx 2100$ Å^3. Using nickel-filtered (0.0095-in. filter) copper Kα radiation (λ 1.5418 Å), 15 lattice points were well centered. These were used to calculate cell parameters and generate settings for the Picker automatic diffractometer.[7]

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(1) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

(2) (a) J. A. Fetchin, Ph.D. Thesis, Case Western Reserve University, 1969; (b) J. P. Fackler, J. A. Fetchin, and D. C. Fries, *J. Amer. Chem. Soc.*, **94**, 7323 (1972).

(3) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *ibid.*, **90**, 2784 (1968).

(4) The perthiocarboxylate ligand is properly named a trithioperoxyarylate. Abbreviations used in this paper are: dtb = dithiobenzoate, $C_6H_5CS_2^-$; p-dtt = dithio-p-toluate, $CH_3C_6H_4CS_2^-$; p-dtc = dithio-p-cumate, $C_3H_7C_6H_4CS_2^-$; dtbS = perthiobenzoate, $C_6H_5CS_3^-$; p-dttS = perthio-p-toluate, $CH_3C_6H_4CS_3^-$; p-dtcS = perthio-p-cumate, $C_3H_7C_6H_4CS_3^-$.

(5) J. P. Fackler, *J. Amer. Chem. Soc.*, **94**, 1009 (1972).

(6) Thanks are extended to J. A. Fetchin for the synthesis of these materials, the details of which are reported elsehwere.[2,3]

(7) See ref 5 for a list of the programs used.

TABLE I

INFRARED AND RAMAN SPECTRA OF DITHIO- AND PERTHIOCUMATE COMPLEXES[a]

$Ni(p\text{-}dtc)_2$	$Pd(p\text{-}dtc)_2$	$Zn(p\text{-}dtc)_2$		Assignments
		Infrared	Raman	
2963 (s)	2972 (m)	2960 (m)		ν(C–H)
2908 (w, br)	2891 (w)	2872 (vw)		
2871 (w)				
1599 (s)	1600 (s)	1600 (s)	1601 (s)	ν(C–C) of phenyl
1462 (w)	1464 (w)	1465 (w, br)	1499 (vw)	
1418 (w)	1420 (w)	1409 (m)		
1385 (vvw)	1383 (vw)			$\rho(CH_3)$
1365 (vvw)	1370 (vw)			
1344 (vw)	1345 (vw)			
1305 (vw)		1309 (vw)		
1276 (s)	1274 (s)	1245 (s)	1252 (s)	ν(phenyl–C)
1232 (vw)	1240 (w)	1230 (vw, br)		$\omega(CH_3)$
1180 (s)	1183 (s)	1186 (s)	1193 (w)	$\omega(CH_3)$ + ρ(C–H)
1146 (w)	1142 (vw)	1136 (vw)		
1099 (w)	1101 (w)	1082 (vw)		ρ(C–H)
1059 (w)	1061 (m)	1059 (vw)		
1015 (w)				
987 (s)	990 (s)	992 (s)		
983 (s)	982 (s)			ν_{as}(C–S)
951 (m)	950 (s)	924 (m, br)		ν_s(C–S)
844 (m, sh)	845 (m, sh)	830 (s)		π(C–H) of para-substituted benzene
833 (s)	834 (s)			
753 (w)	751 (w)	745 (vw)	747 (vw)	
740 (vw)	727 (vvw)	727 (vw)	734 (vw)	
634 (vw)	635 (vvw)			
602 (w)	604 (vvw)	606 (vw)	600 (vvw)	
578 (w)	575 (vvw)	580 (vw)	580 (vvw)	
507 (w)	509 (w)	483 (vvw)		$\delta(CH_3)$
424 (vw)	426 (vw)	465 (vvw)		π(phenyl ring)
370 (m)	341 (m)	302 (w)		ν(M–S)
			160 (w)	

$Ni(dtc)_2S$	$Ni(dtc)_2S_2$	$Pd(dtc)_2S$	$Pt(dtc)_2S$	$Zn(dtc)_2S_2$		Assignment
				Infrared	Raman	
2962 (m)	2960 (w)	2968 (m)	2966 (s)	2961 (s)		ν(C–H)
2932 (w, br)			2934 (w, sh)	2930 (w)		
2872 (w)	2872 (vvw)	2875 (w, sh)	2873 (w)	2871 (w)		
1598 (m)	1603 (s)	1599 (s)	1601 (s)	1598 (s)	1597 (s)	ν(C–C) of phenyl + $\rho(CH_3)$
1498 (w)	1503 (w)		1498 (w)		1498 (m)	
1464 (m)	1465 (m)	1465 (m)	1462 (m)	1453 (w)		
	1454 (m)					
1413 (w)	1420 (m)	1415 (m, sh)	1410 (m)	1415 (m)		
1384 (vw)	1386 (vw)	1387 (vw)				
1366 (vw)	1365 (w)	1365 (vw)	1363 (w)	1364 (m)		
1338 (w)	1343 (w)	1340 (w)	1340 (w)	1337 (w)		
1307 (w)	1305 (w)	1308 (w)		1306 (w)		
1278 (s)	1284 (m)	1279 (m)	1282 (s)	1241 (s)	1240 (s)	ν(phenyl–C)
1253 (vw, sh)	1245 (s)	1240 (w, sh)		1235 (s)	1233 (s)	
					1223 (sh)	
1182 (s)	1188 (s)	1182 (s)	1184 (s)	1188 (s)	1188 (vs)	ρ(C–H) + $\rho(CH_3)$
1139 (vw)	1150 (vw)	1140 (w)	1145 (w)	1144 (w)	1144 (vw)	
1130 (vvw)	1122 (vw)	1130 (vw, sh)			1127 (vw)	
1098 (vw)	1100 (vw)	1102 (w)	1100 (w)	1100 (w)	1101 (w)	
1063 (w)	1060 (s)	1063 (w)	1059 (m)	1065 (m)	1060 (w)	
1021 (s)	1035 (s, br)	1032 (s)	1032 (s)	1024 (s, br)	1025 (m)	$\nu(C\text{–}S_1)$
		1027 (s)	1020 (m, sh)			
991 (s)		992 (s)	1002 (s)			ν_{as}(C–S)
			991 (s)			
954 (m)		955 (s)	958 (m)	963 (w)?		ν_s(C–S)
927 (vw)	927 (w)	924 (vw)	924 (w)	908 (w)	905 (s)	$\nu(C\text{–}S_2)$
		893 (vw)?				π(C–H) of para-substituted benzene + $\delta(CH_3)$ + π(phenyl ring)
836 (s)	830 (s)	838 (s)	832 (s, br)	837 (s)	823 (vw)	
826 (s)	834 (s)	828 (s)		825 (s)		
752 (w)	751 (w)	753 (m)	753 (m)	747 (w)	746 (s)	
734 (vw)	739 (w, sh)	734 (w)			735 (vw)	
636 (vw)	639 (w)	638 (w)	638 (w)	635 (w)	636 (vw)	
600 (w)	600 (vw)	602 (m)	599 (w)	597 (w)	599 (m)	
564 (m)	567 (s)	566 (m)	577 (m)	573 (m)	571 (w)	
530 (w)	526 (m)	523 (w)	522 (w)	546 (s)	546 (w)	
509 (w)	508 (m)	512 (m)	506 (w)	511 (w)		
				488 (w)	487 (m)	ν(S–S)
429 (w)	435 (w)	432 (m)	447 (w)		454 (m)	π(phenyl ring)
			420 (vw)		403 (w)	
384 (w)	378 (w, br)	335 (s)	351 (w)	385 (w)		ν(M–S) + bending modes
	365 (w, br)	310 (vw)		351 (w)		
	272 (w)			323 (m)	322 (vw)	
					302 (vw)	
					282 (w)	

[a] All values are in cm^{-1}. Key: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. Values in parentheses are depolarization ratios (in carbon disulfide solution).

TABLE II

INFRARED SPECTRAL BANDS OF $[\mathrm{Pt(dtb)_2}]_2$, $[\mathrm{Pt}(p\text{-dtt})_2]_2$, AND $[\mathrm{Pt}(p\text{-dtc})_2]_2$

$[\mathrm{Pt(dtb)_2}]_2$	$[\mathrm{Pt}(p\text{-dtt})_2]_2$	$[\mathrm{Pt}(p\text{-dtc})_2]_2$	Assignment
		2965 (m)	ν(C–H)
		2932 (w)	
		2880 (w)	
1590 (w)	1602 (s)	1601 (m)	ν(C–C) of phenyl
1483 (vw)	1500 (vvw)	1470 (w)	
1443 (m)	1455 (vvw)	1416 (w)	
1330 (vvw)	1411 (vw)	1360 (w)	
1311 (vw)	1309 (w, sh)		
1275 (m)	1288 (s)	1286 (s)	ν(phenyl–C) (terminal)
	1274 (sh)		
1223 (m)	1223 (w)	1227 (w)	ν(phenyl–C) (bridging)
1181 (w)	1180 (s)	1185 (s)	ρ(C–H) + ρ(CH$_3$)
1106 (vw)			
1085 (vw)			
	1128 (vw)	1060 (m)	
1044 (s)	1035 (m, br)	1036 (m)	ν(C=S) (bridging)
1030 (sh)		1020 (w, sh)	
1016 (sh)			
1000 (vw)	1007 (w)		Ring breathing
971 (vw)	972 (sh)	998 (w)	ν_{as}(C–S)(terminal)
949 (vw)	955 (m)	959 (w)	ν_s(C–S)(terminal)
907 (w)	913 (w)	918 (w)	ν(C–S)(bridging)
843 (vw, br)	818 (s)	839 (s)	π(C–H) of para-substituted benzene
758 (s)	789 (vw)	755 (w)	
	710 (vw)		
686 (m)			
665 (vw)		638 (vw)	
653 (w)	635 (vw)	632 (vw)	
568 (vw)	698 (w)	598 (vw)	
	570 (w)	576 (w)	
	450 (w)	515 (vw)	π(phenyl ring)
	404 (vw)	448 (vw)	
	317 (vvw)	282 (vvw)	ν(M–S)(?)

TABLE III

FRACTIONAL ATOMIC COORDINATES AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $[\mathrm{Pt}(p\text{-dtc})_2]_2$

Atom	x/a	y/b	z/c
Pt1	0.05290 (10)	−0.12840 (10)	−0.28531 (11)
Pt2	0.02273 (9)	−0.02616 (9)	−0.12765 (11)
S1	0.0104 (6)	−0.1507 (7)	−0.0228 (8)
S2	0.0125 (6)	0.0858 (6)	−0.2448 (7)
S3	−0.1848 (6)	−0.1138 (6)	−0.2720 (8)
S4	0.2318 (6)	0.0912 (6)	0.0102 (7)
S5	0.2308 (6)	0.0492 (7)	−0.2240 (7)
S6	−0.1285 (7)	−0.3056 (7)	−0.3686 (8)
S7	0.1574 (7)	−0.1585 (7)	−0.1138 (8)
S8	−0.0848 (6)	−0.1461 (6)	−0.4832 (7)
C17	0.0970 (2)	−0.184 (3)	−0.022 (3)
C11	0.127 (2)	−0.238 (3)	0.069 (3)
C12	0.122 (3)	−0.325 (3)	0.025 (3)
C13	0.155 (3)	−0.377 (2)	0.113 (4)
C14	0.192 (3)	−0.341 (4)	0.230 (4)
C15	0.201 (3)	−0.248 (3)	0.280 (4)
C16	0.162 (3)	−0.201 (3)	0.193 (3)
C117	0.228 (4)	−0.395 (4)	0.323 (4)
C45	0.300 (2)	0.118 (2)	−0.073 (2)
C41	0.434 (2)	0.212 (2)	0.005 (3)
C42	0.491 (2)	0.292 (3)	0.117 (3)
C43	0.618 (3)	0.368 (3)	0.187 (3)
C44	0.691 (3)	0.373 (3)	0.152 (3)
C46	0.632 (3)	0.295 (3)	0.040 (3)
C47	0.507 (2)	0.216 (2)	−0.042 (3)
C145	0.836 (3)	0.455 (3)	0.238 (3)
C68	−0.194 (3)	−0.279 (3)	−0.502 (3)
C62	−0.317 (3)	−0.351 (3)	−0.599 (3)
C63	−0.363 (3)	−0.334 (3)	−0.712 (3)
C64	−0.484 (3)	−0.410 (3)	−0.815 (3)
C65	−0.567 (3)	−0.518 (3)	−0.812 (3)
C66	−0.520 (3)	−0.534 (3)	−0.699 (3)
C67	−0.403 (3)	−0.454 (3)	−0.596 (3)
C168	−0.693 (3)	−0.602 (3)	−0.929 (3)
C23	−0.144 (2)	−0.010 (3)	−0.320 (2)
C21	−0.221 (3)	0.002 (3)	−0.434 (2)
C22	−0.348 (4)	−0.079 (4)	−0.491 (4)
C24	−0.428 (4)	−0.070 (4)	−0.601 (4)
C26	−0.261 (3)	0.097 (3)	−0.576 (4)
C27	−0.177 (2)	0.090 (3)	−0.473 (3)
C25	−0.383 (4)	0.019 (3)	−0.635 (4)
C123	−0.489 (5)	0.011 (5)	−0.757 (5)
C68A	−0.694 (4)	−0.621 (4)	−1.049 (4)
C68B	−0.776 (4)	−0.567 (4)	−0.940 (4)
C45A	0.885 (3)	0.561 (3)	0.327 (4)
C45B	0.876 (5)	0.393 (5)	0.319 (5)
C23A	−0.531 (4)	0.063 (4)	−0.702 (5)
C23B	−0.454 (6)	0.045 (6)	−0.847 (6)
C17A	0.216 (5)	−0.391 (5)	0.431 (6)
C17B	0.358 (5)	−0.351 (5)	0.369 (5)

Crystal Data for $\mathrm{Pt_2}(p\text{-dtc})_4$.—$\mathrm{C_{40}H_{44}S_8Pt_2}$: Formula weight 1170; deep green-brown triclinic prism $\sim$0.07 $\times$ 0.15 $\times$ 0.10 mm^3; a = 15.564 (6), b = 15.480 (6), c = 12.555 (3) Å; α = 90.85 (1), β = 116.80 (1), γ = 122.55 (1)°; V = 2110 Å^3; d_{measd} = 1.7–1.9 (by floatation), d_{calcd} = 1.84 g/cm^3; μ(Cu Kα) = 88.1 cm^{-1}; Z = 2.

Determination and Refinement of Structure

The X-ray data were collected by the θ–2θ scan technique at a rate of 2°/min, over a complete hemisphere of the reciprocal lattice, on the four-circle goniostat. In this manner 5209 reflections were obtained with intensities greater than background. Reduction of these data taking into account Lorentz and polarization effects followed.[7] In view of the elongated shape of the crystal and the linear absorption coefficient of 87.08 cm^{-1}, absorption corrections were made.[7] Transmission coefficients ranged from 0.29 to 0.71. Isotropic refinement was pursued with 4225 unique nonzero reflections to R_1 = 0.15. Additional refinement was carried out on 3459 reflections with $I/\sigma I > 3.0$.

The platinum atom positions for $\mathrm{Pt_2}(p\text{-dtc})_4$ were located using heavy-atom techniques from an origin removed Patterson synthesis. After several cycles of structure factor Fourier calculations the sulfur atoms and most carbon atoms were located. Full-matrix least-squares refinement followed by additional structure factor Fourier calculations positioned the remaining carbon atoms. Isotropic refinement for the 50 nonhydrogen atoms using unit weights for all reflections converged at R = 0.125 with a Pt–Pt distance of 2.87 Å.

Anisotropic refinement including anomalous dispersion corrections[8] for the platinum and sulfur atoms along with isotropic refinement of the 40 carbon atoms was pursued. It was considered complete when the shift/error for all platinum and sulfur atom positional parameters was less than 0.5 and less than 1.0 for all other parameters except the temperature factors for the isopropyl carbon atoms. Even for these latter carbon atoms the shift/error was less than 2.0 in the last cycle with reasonable values being obtained. Further refinement was considered unwarranted in view of the computer time required. A final weighting scheme was calculated in the form $w = [a + bF_o + c|F_o|^2]^{-1}$, where $a = -1.35$, $b = 0.651$, $c = 0.013$ as obtained from a plot of $|\Delta F|$ vs. $|F_o|$. The R_1 and R_2 values obtained are 0.099 and 0.125, respectively. A full-data difference Fourier revealed residual electron density to be less than 1 electron/Å^3 except in the vicinity of the plainum atoms where it was slightly larger. Positional and temperature parameters are listed in Tables III and IV, respectively, with their estimated standard deviations.[9]

Vibrational Spectra of the Nickel, Palladium, and Zinc Dithioarylates

The vibrational spectra of the dithiocumate complexes of nickel(II), palladium(II), and zinc(II) and

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(8) Scattering factor tables for the nonhydrogen atoms were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965). Real and imaginary components of the anomalous dispersions were those of D. T. Cromer, *ibid.*, **18**, 17 (1965).

(9) Tables of structure factors and spectra of Ni, Pd, and Zn dithiobenzoate and dithiotoluate complexes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3000. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE IV
THERMAL PARAMETERS

Anisotropic

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt1	0.00801 (11)	0.00545 (11)	0.00753 (14)	0.00424 (9)	0.00360 (10)	0.00267 (10)
Pt2	0.00595 (10)	0.00583 (11)	0.00907 (15)	0.00457 (8)	0.00332 (9)	0.00375 (11)
S1	0.0090 (7)	0.0080 (7)	0.0117 (9)	0.0065 (5)	0.0055 (6)	0.0060 (7)
S2	0.0065 (5)	0.0065 (6)	0.0102 (8)	0.0045 (5)	0.0032 (5)	0.0045 (6)
S3	0.0068 (6)	0.0069 (6)	0.0109 (9)	0.0050 (5)	0.0044 (6)	0.0046 (7)
S4	0.0067 (6)	0.0060 (5)	0.0081 (7)	0.0048 (5)	0.0032 (5)	0.0024 (6)
S5	0.0075 (6)	0.0069 (7)	0.0074 (8)	0.0038 (5)	0.0036 (6)	0.0028 (6)
S6	0.0104 (8)	0.0056 (6)	0.0109 (9)	0.0034 (6)	0.0033 (7)	0.0039 (7)
S7	0.0103 (7)	0.0073 (6)	0.0088 (8)	0.0071 (5)	0.0056 (6)	0.0038 (6)
S8	0.0075 (6)	0.0052 (5)	0.0084 (8)	0.0033 (5)	0.0033 (6)	0.0023 (6)

Isotropic

Atom	B	Atom	B	Atom	B	Atom	B
C123	10.4 (14)	C11	4.1 (5)	C43	4.8 (6)	C67	4.8 (6)
C68A	6.4 (11)	C12	5.9 (7)	C44	4.6 (6)	C168	5.6 (7)
C68B	7.5 (11)	C13	5.7 (7)	C46	3.8 (5)	C23	3.9 (5)
C45A	6.3 (8)	C14	5.7 (7)	C145	5.4 (7)	C21	4.2 (6)
C45B	7.9 (14)	C15	6.0 (8)	C68	4.2 (6)	C22	7.3 (9)
C23A	8.5 (12)	C16	5.7 (7)	C62	4.3 (6)	C24	7.9 (10)
C23B	10.4 (18)	C117	7.6 (10)	C63	5.4 (7)	C26	6.1 (8)
C17A	9.8 (16)	C45	3.1 (4)	C64	5.1 (7)	C27	4.0 (5)
C17B	7.1 (13)	C41	3.7 (5)	C65	4.7 (6)	C25	7.1 (9)
		C42	4.7 (5)	C66	5.4 (7)		

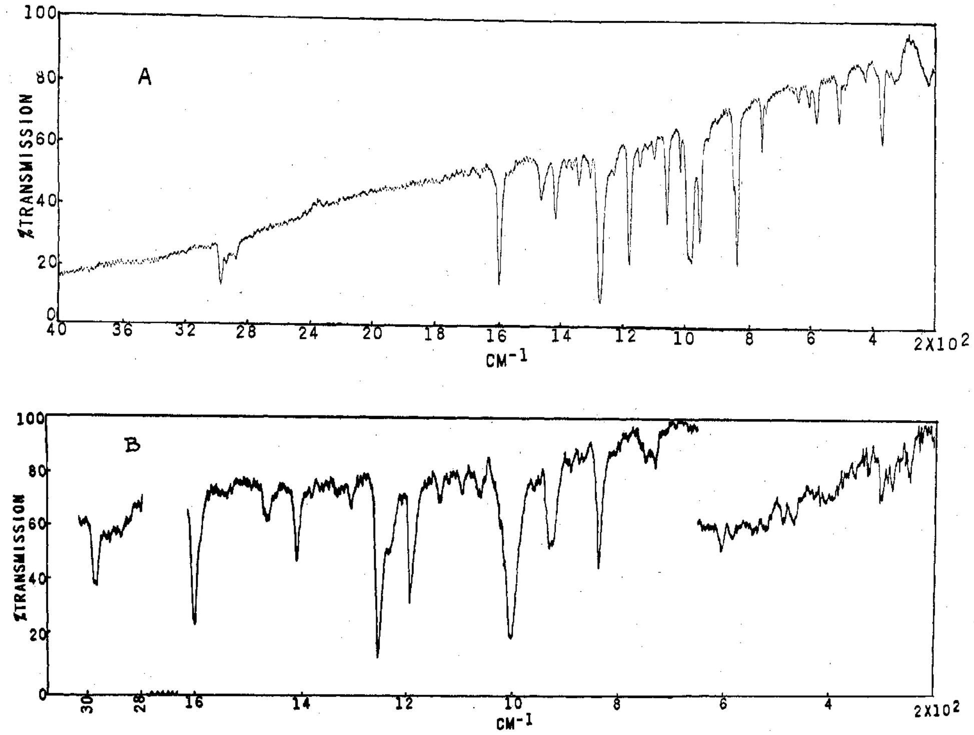

Figure 1.—Vibrational spectra of some bis(dithiocumato)metal complexes: (A) infrared spectrum of Ni(p-dtc)$_2$ (CsBr pellet); (B) infrared spectrum of Zn(p-dtc)$_2$ (CsI pellet).

their sulfur addition products are presented[9] in Table I. Spectra of selected complexes[10] are presented in Figures 1 and 2. The assignments of the vibrations associated with the aromatic group are made by consulting standard texts[11,12] and will not be discussed here. Instead, only the vibrations associated with the chelate rings will be presented.

Phenyl–Carbon Stretching Frequency.—The phenyl–carbon stretching frequency, S_2C–Ar, occurs between 1245 and 1251 cm^{-1} in the dithioaryl acid complexes of zinc(II), and between 1265 and 1289 cm^{-1} in the nickel(II) and palladium(II) complexes. This band remains essentially unchanged upon forming the mixed ligand perthiodithioarylate complexes (although a shoulder is observed on the low-frequency side of the band in some cases) and shifts 25 cm^{-1} to lower frequencies in the bis(perthioarylate) species.

In all cases studied the phenyl–carbon stretching mode occurs at a frequency lower than that observed for carbon–carbon double bonds (~1600 cm^{-1} in most cases) but higher than that usually observed[12] for car-

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(10) The Ph.D. thesis of J. M. Burke, Case Western Reserve University, 1971 should be consulted for other spectra.

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

(12) N. B. Coltup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

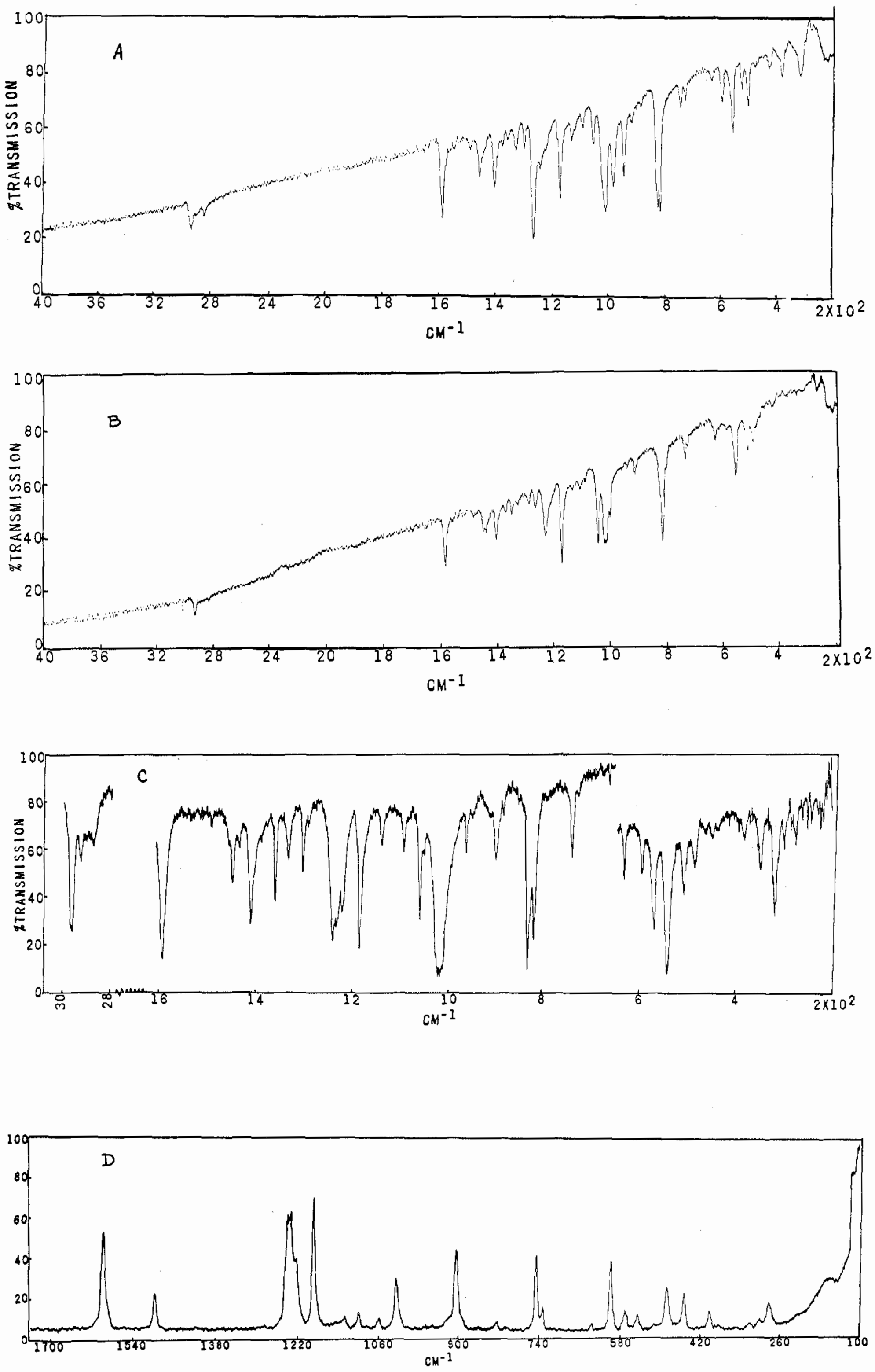

Figure 2.—Vibrational spectra of some dithiocumatoperthiocumato and bis(perthiocumato)metal complexes: (A) infrared specspectrum of Ni(*p*-dtcS)(*p*-dtc) (CsBr pellet); (B) infrared spectrum of Ni(*p*-dtcS)$_2$ (CsBr pellet), (C) infrared spectrum of Zn(*p*-dtcS)$_2$ (CsI pellet); (D) Raman spectrum of Zn(*p*-dtcS)$_2$.

bon–carbon single bonds (993 cm^{-1} in ethane). The band in the bis(dithioaryl acid) complexes is also at a higher frequency than that reported by Savant, *et al.*,[13] for the bis(monothiobenzoato)nickel(II) and -zinc(II) (1225 cm^{-1} in both cases).

Carbon–Sulfur Stretching Frequencies.—All expected carbon–sulfur stretching frequencies occur between 900 and 1100 cm^{-1} in the compounds studied here. The assignments of the frequencies arise from consideration of several factors. Structural work on both bis(perthiocumato)zinc(II)[2b] and perthiocumatodithiocumatonickel(II),[2b,14] as well as that of bis(per-

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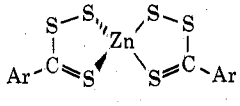
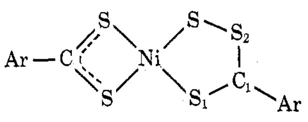
[13] V. V. Savant, J. Gopalakrishnan, and C. C. Patel, *Inorg. Chem.*, **9**, 748 (1970).

[14] D. C. Fries and J. P. Fackler, Jr., *Chem. Commun.*, 276 (1971).

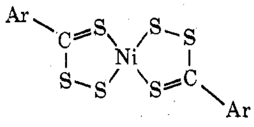
thiobenzoate)nickel(II) and -zinc(II),[15] show that these species can be represented by structures V, VI, and VII, respectively. For purposes of making assignments, we presume that the geometry around the metal atom has little effect on the carbon–sulfur stretching frequencies (as evidenced by the small differences between the spectra of the Zn complexes and those of the Ni, Pd, and Pt complexes). Spectral changes are observed as an extra sulfur atom is added to each ligand. For example, in the 900–1100-cm^{-1} region two bands, at 985 and 951 cm^{-1}, are found in Ni(p-dtc)$_2$, while four bands, at 1021, 991, 954, and 927 cm^{-1}, are present for Ni(p-dtcS)(p-dtc). Again only two bands, at 1035 and 927 cm^{-1}, are observed in this region for Ni(p-dtcS)$_2$ (Table I and Figures 1 and 2).



V



VI



VII

By comparison with spectra of similar compounds[16] one of the two bands in Ni(p-dtc)$_2$ between 900 and 1100 cm^{-1} can be attributed to a carbon–sulfur asymmetric stretching frequency. If the other band in this region in Ni(p-dtc)$_2$ is assigned to the symmetric carbon–sulfur stretching vibration, it can be assumed that, as the chelate ring is expanded by the addition of a sulfur atom, II, four stretching modes should be found (two due to the four-membered ring and two due to the five-membered ring), as observed between 900 and 1100 cm^{-1} in Ni(p-dtcS)(p-dtc). The two carbon–sulfur bands (991 and 954 cm^{-1}) attributed to the four-membered ring remain essentially unchanged from those found in Ni(p-dtc)$_2$, while the band at 1021 cm^{-1} can be attributed to the C_1–S_1 stretch, VI, and the band at 927 cm^{-1} to the C_1–S_2 stretch. When both chelate rings of Ni(p-dtc)$_2$ are expanded by one sulfur atom to form Ni(p-dtcS)$_2$ (VII) the bands appearing between 900 and 1100 cm^{-1} have frequencies close to the values of the carbon–sulfur stretches of the five-membered ring in the mixed-ligand species.

In the other "sulfur-poor" mixed ligand and "sulfur-rich" complexes studied, the same effect is noted, namely the presence of two bands separated by ~50 cm^{-1} in the "sulfur-poor" species, four bands in the mixed ligand complexes and two bands separated by ~100 cm^{-1} in the "sulfur-rich" compounds.

The assignment of the lower and weaker frequency in the carbon–sulfur stretching region of the bis(dithioarylato)metal species to the carbon–sulfur symmetric stretch is in agreement with assignments[16] made previously for similar compounds. The intensity of this band is medium to strong in the Raman spectra of the zinc complexes, while the asymmetric carbon–sulfur stretching frequency is unobserved in the Raman, a result which further substantiates the assignments presented.

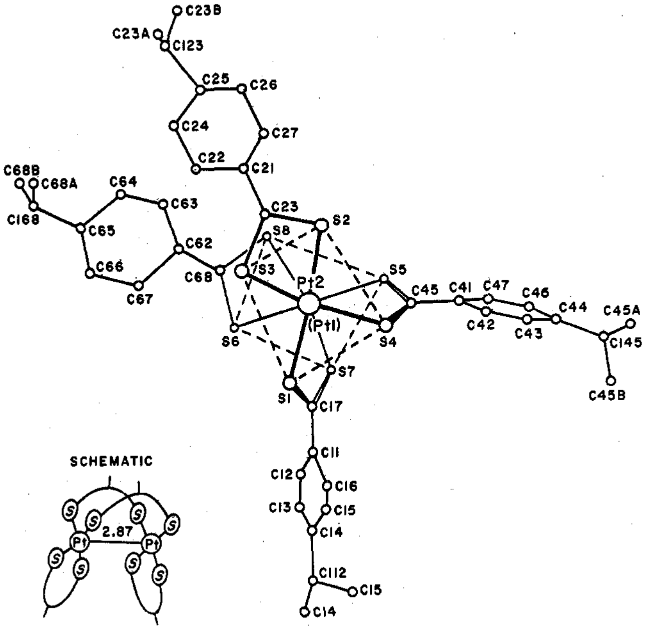


Figure 3.—Sketch of the geometry of Pt$_2$(p-dtc)$_4$.

Since X-ray crystallographic studies[17,18] have shown that bis(dithiobenzoato)nickel(II) and -palladium(II) are stacked trimers in the solid state, it could be assumed that the two bands in the 900–1000-cm^{-1} region arise from the splitting of a single band, due to intermolecular interactions. However, this is unlikely. Solid-state interactions would have to produce the observed 30-cm^{-1} separation, leaving both bands sharp. Furthermore, the bands are not shifted either in intensity or in position in CHCl$_3$, where intermolecular interactions are expected to be diminished or removed entirely by complete dissociation[19] of the trimers.

Sulfur–Sulfur Stretching Vibrations.—The 400–600-cm^{-1} region of the spectra of metal dithioarylates contains bands which shift upon addition of sulfur to the chelate ring. It was proposed[2,3] that the appearance of one or two bands of medium to strong intensity in the infrared region from 520 to 570 cm^{-1} was indicative of the S–S stretching vibration. However, this would be a relatively high frequency for a S–S vibration,[12] since the dipole moment change must be rather small. The S–S stretching frequency in similar perthio species[20] absorbs in the infrared at 480 cm^{-1}.

The Raman spectra of the zinc–perthio complexes lead to an alternate and presumably better assignment for the S–S stretching frequency. A band of medium to strong intensity at 480 cm^{-1} in the Raman spectra of the zinc–perthio complexes can be assigned to ν(S–S). The infrared counterpart of this band is absent or very weak. The bands observed in the 520–570-cm^{-1} region in these "sulfur-rich" complexes then are assigned to an out-of-plane bending mode of the H atoms plus a torsional twist of the phenyl ring.[12] These vibrations are probably less restricted in the perthio spe-

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[15] M. Bonamico, G. Dessy, G. Fares, and L. Scaramuzza, *J. Chem. Soc. A*, 20, 3191 (1971).

[16] G. W. Watt and B. J. McCormick, *Spectrochim. Acta*, **21**, 753 (1965); J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistilehti B*, **29**, 75 (1956).

[17] M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 324 (1969).

[18] M. Bonamico and G. Dessy, *ibid.*, 483 (1968).

[19] C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968).

[20] D. Coucouvanis and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **89**, 1346 (1967).

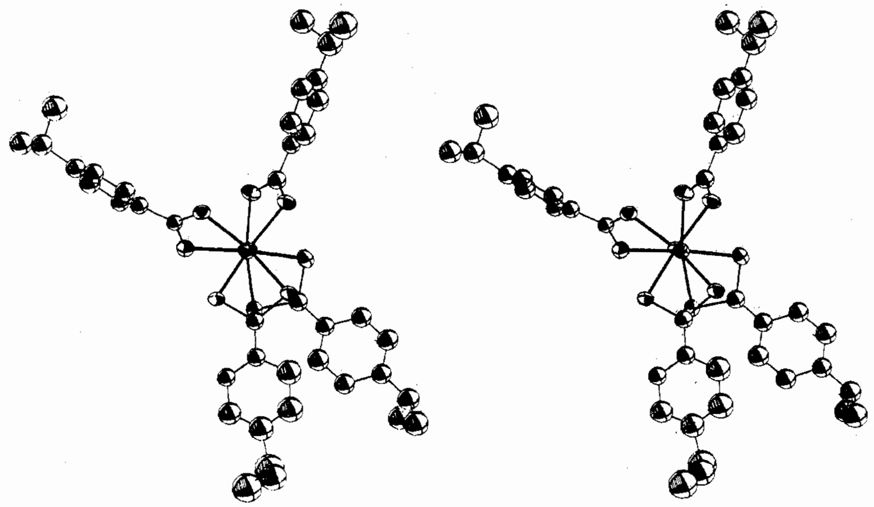

Figure 4.—Stereo pair with thermal elipsoids at 50% probability density for the structure of Pt$_2$(p-dtc)$_4$.

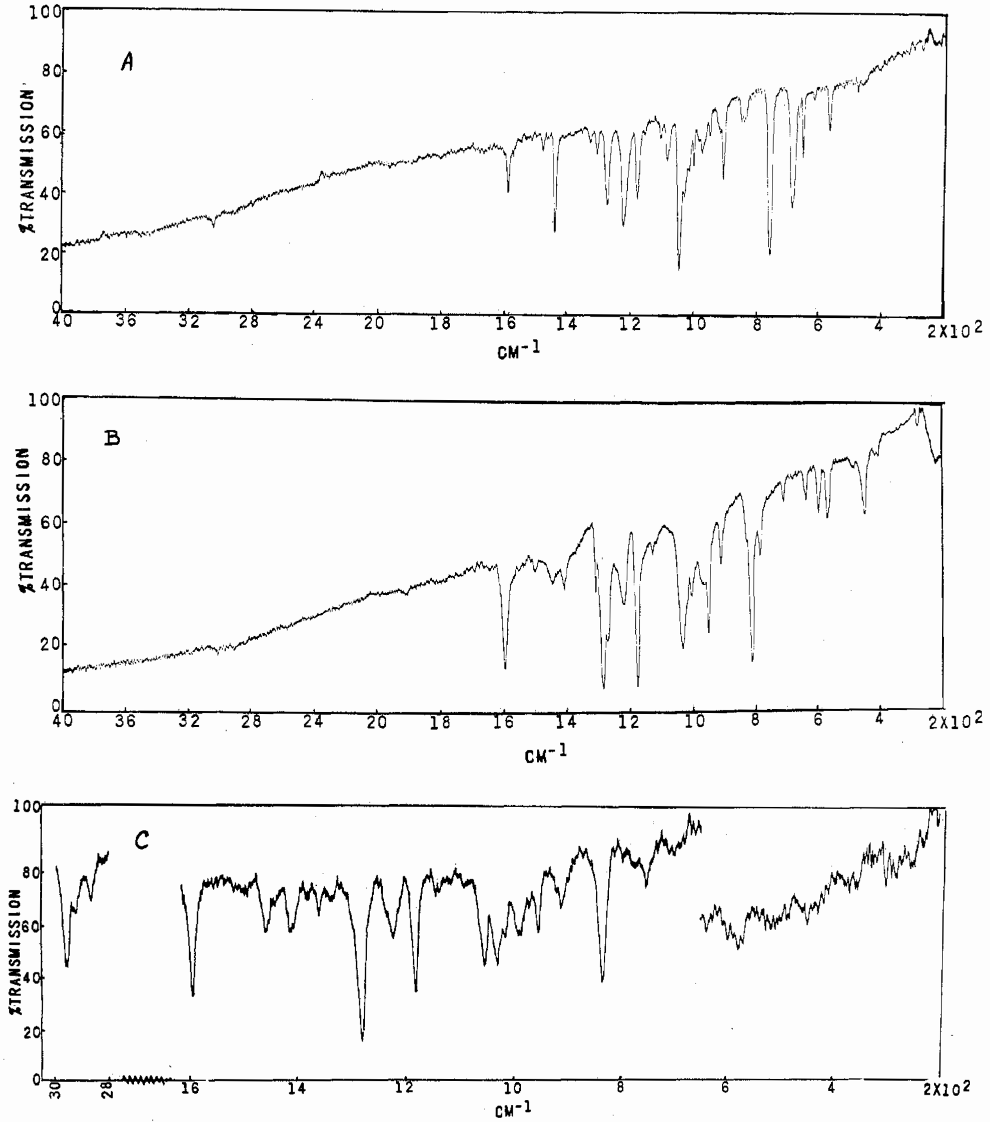

Figure 5.—Vibrational spectra of the bis(dithioaryl acid)platinum dimers: (A) infrared spectrum of [Pt(dtb)$_2$]$_2$ (CsI pellet); (B) infrared spectrum of [Pt(p-dtt)$_2$]$_2$ (CsBr pellet); (C) infrared spectrum of [Pt(p-dtc)$_2$]$_2$ (CsI pellet).

cies than in the dithio species where the phenyl groups are coplanar with the chelate rings.[2b,14,15]

Additional support for the above assignment comes from the fact that no bands are observed in the 520–570-cm^{-1} region in the "sulfur-rich" platinum(II) complex of 3,4,5-trimethoxydithiobenzoate, while bands in this region are observed in the "sulfur-poor" Pt(p-dtc)$_2$[(C$_6$H$_5$)$_2$PCH$_3$]. One phenyl ring in this latter

Table V

Bond Lengths in $Pt_2(p\text{-dtc})_4$

Pt1–Pt2	2.870 (2)	Pt2–S1	2.314 (9)
Pt1–S5	2.333 (7)	Pt2–S2	2.311 (9)
Pt1–S6	2.304 (7)	Pt2–S3	2.321 (7)
Pt1–S7	2.281 (9)	Pt2–S4	2.284 (6)
Pt1–S8	2.320 (8)	C17–C11	1.48 (5)
S1–C17	1.68 (5)	C11–C12	1.40 (7)
S2–C23	1.70 (2)	C11–C16	1.39 (6)
S3–C23	1.68 (4)	C12–C13	1.43 (7)
S4–C45	1.71 (4)	C13–C14	1.29 (6)
S5–C45	1.65 (3)	C14–C15	1.47 (8)
S6–C68	1.71 (4)	C14–C117	1.51 (8)
S7–C17	1.71 (4)	C15–C16	1.40 (7)
S8–C68	1.71 (3)	C117–C17A	1.45 (10)
		C117–C17B	1.52 (9)
C23–C21	1.42 (5)	C45–C41	1.48 (3)
C21–C22	1.39 (5)	C41–C42	1.38
C21–C27	1.36 (5)	C41–C47	1.46 (6)
C22–C24	1.45 (7)	C42–C43	1.37 (4)
C24–C25	1.34 (7)	C43–C44	1.36 (7)
C26–C27	1.43 (6)	C44–C46	1.36 (5)
C26–C25	1.34 (5)	C44–C145	1.57 (4)
C25–C123	1.61 (8)	C46–C47	1.37 (3)
C123–C23A	1.59 (13)	C145–C45A	1.53 (7)
C123–C23B	1.45 (12)	C145–C45B	1.56 (9)
		C68–C62	1.38 (3)
		C62–C63	1.37 (5)
		C62–C67	1.42 (4)
		C63–C64	1.39 (3)
		C64–C65	1.45 (5)
Some nonbonded distances		C65–C66	1.37 (5)
S4–S7	3.48 (3)	C65–C168	1.50 (3)
S4–S5	3.00 (3)	C66–C67	1.37 (3)
S2–S8	3.73 (4)	C168–C68A	1.52 (8)
		C168–C68B	1.60 (10)

Table VI

Selected Angles and Planes in $Pt_2(p\text{-dtc})_4$

Atoms	Angles, deg	Planes
S6–Pt1–S8	73.9 (5)	
S5–Pt1–S8	100.8 (4)	
S6–Pt1–S7	92.8 (5)	Angle between[a] S5–S6–S7–S8 and S1–S2–S3–S4 12.5°
S5–Pt1–S7	92.0 (5)	
S3–Pt2–S2	73.2 (4)	
S3–Pt2–S1	100.8 (5)	Angle between[b] S2–S3–C23–C21 and C21 ring 2.2°
S2–Pt2–S4	96.5 (5)	
S1–Pt2–S4	89.5 (5)	
S4–C45–S5	125.5 (2.6)	Angle between[b] S4–S5–C45–C41 and C41 ring 21.7°
S6–C68–S8	108.3 (2.3)	
S1–C17–S7	126.6 (2.3)	
S2–C23–S3	109.5 (2.0)	

Distance (Å) of Platinum Atoms from Sulfur Atom Planes

S5–S8 plane	Pt1 −0.104	Pt2 −2.946
S1–S4 plane	Pt1 2.914	Pt2 0.0539

[a] Standard deviation from plane 0.005 A. [b] Phenyl rings have standard deviations of 0.02 Å from plane.

compound is twisted nonplanar to the MSCS portion of the complex.[21]

Metal–Sulfur Stretching Vibrations.—The region between 200 and 400 cm^{-1} contains the metal–sulfur stretching frequencies. These bands are assigned by comparison with spectra of similar compounds,[22,23] and appear at ~370 cm^{-1} for the nickel(II) complexes, ~340 cm^{-1} for the palladium(II) species, and between 300 and 400 cm^{-1} for the "sulfur-poor" zinc complexes.

Chelate Ring Vibrations.—The assignments of the chelate ring vibrations are at best tentative. They are made by observing which bands shift as sulfur is added to the bis(dithioarylato)metal complex. It is possible that these bands could be assigned to vibrations within the aromatic group.

Dimeric Platinum Complexes.—The X-ray crystallographic structure of $Pt_2(p\text{-dtc})_4$ shows the dimeric arrangement presented in Figure 3. Tables V and VI present bond lengths and selected bond angles, respectively. A stereo pair presentation of the structure is seen in Figure 4.

The short platinum–platinum distance of 2.87 Å compared with a Pt–Pt distance of 3.23 and 3.25 Å respectively in bis(dimethylglyoximato)platinum(II) and $[Pt(NH_3)_4]PtCl_4$[24–26] is particularly striking and leads to the suggestion that considerable metal–metal bonding occurs (*vide infra*). The fact that the platinum(II) atoms are closer to each other by 0.15 Å than the distance between the centers of the two S_4 planes, Table VI, further strengthens this conclusion.

Infrared Spectra of Platinum Dimers.—An examination of the data in Table II and Figure 5 shows striking similarities between the spectrum of $Pt_2(p\text{-dtc})_4$ and the spectra of $Pt(p\text{-dtt})_2$ and $Pt(dtb)_2$. The spectra of $Pt_2(p\text{-dtc})_4$ and $Pt(dtt)_2$ are almost identical in the ν(Ph–C) and ν(C–S) regions, not only in band positions but also in band intensities. The band intensities for $Pt(dtb)_2$ are slightly different but the positions are very similar.

From the infrared data it appears that $Pt(dtb)_2$ and $Pt(dtt)_2$ are dimers[27] similar in structure to $Pt_2(p\text{-dtc})_4$. In this latter molecule there are different bridging and terminal dithiolate ligands. The bridging ligands show an S–C–S angle approximately 17° larger than the same angle in the two terminal ligands. The assignments made in Table II take this into account. In fact, the terminal ligands are spectrally similar to those found in $Ni(p\text{-dtc})_2$, $Pd(p\text{-dtc})_2$, $Zn(p\text{-dtc})_2$, and the other *p*-dithiocumate complexes studied. The remaining bands in the C–Ph and C–S regions can be assigned to bridging ligands. The lower ν(C–Ph) stretch in the bridging ligands compared with the terminal ones is expected from the ~0.10 Å longer bond lengths found (Table V) for these ligands.

It is significant that no well-defined Pt–S bands could be found in the vibrational spectra of any of these platinum dithioarylates. While such bands are often weak,[23] they are usually easily observed. The metal–metal interaction in these dimers may shift the Pt–S frequency below 200 cm^{-1} or otherwise drastically reduce its intensity. Either effect is possible with significant Pt–Pt bonding.[28]

Bonding to the Platinum(II) Dimers.—While numerous examples of platinum–platinum bonded species have appeared in the recent literature,[26,29–35] none of

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[21] D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.

[22] D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967; J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds," Plenum Press, New York, N. Y., 1971, p 248.

[23] J. M. Burke and J. P. Fackler, Jr., *Inorg. Chem.*, **11**, 2744 (1972). Force constant calculations were made for the ν_{M-S} bands in the trithiocarbonate and perthiocarbonate complexes described.

[24] C. H. Wei and L. F. Dahl, *ibid.*, **9**, 1878 (1970).

[25] R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957).

[26] J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 133 (1962).

[27] Low solubility failed to give us an accurate solution measurement in hydrocarbon solvents.

[28] Kinematically a strong Pt–Pt bond effectively increases the Pt mass, hence lowering ν(Pt–S). A strong Pt–Pt bond can also substantially reduce the Pt–S bond polarity.

[29] M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

[30] F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

[31] K. K. Chenig, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971).

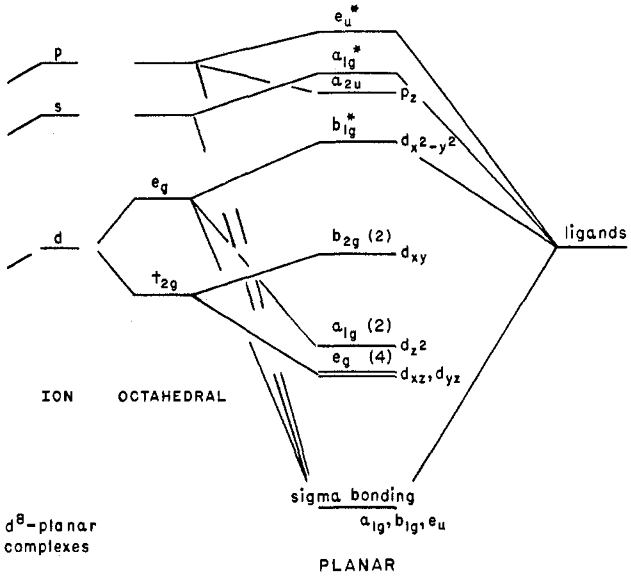

Figure 6.—A typical metal orbital energy-level diagram for a planar d^8 complex.

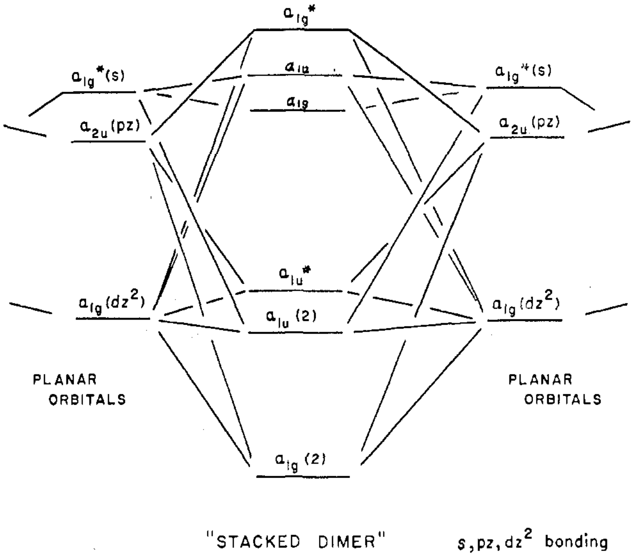

Figure 7.—Energy-level diagram for Pt–Pt σ-bond formation.

these compounds are formally platinum(II), although it has been established that only partial oxidation[35] may lead to significant Pt–Pt bond formation, as in $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$. The metallic conductivity this columnar material displays is very striking. It is thought to arise from partial reduction in the electron populations of the band formed by overlap of the filled d_{z^2} orbitals (Figure 6) on the metal.

In the case of $Pt_2(p\text{-dtc})_4$ metal d_{z^2} and p_z hybridization and overlap leads to four σ orbitals a_{1g}, a_{1u}, a_{1g}^* and a_{1u}^*. Depending on the metal–metal distance and the energy difference between the $5d_{z^2}$ and $6p_z$ functions, a strong σ bond may result, Figure 7. Rundle[25] several years ago described this type of bond as it applied to the columnar species $Pt(NH_3)_4PtCl_4$, bis(dimethylglyoximato)nickel(II), and related nickel triad complexes. This σ bond, however, does not itself account for the cubic antiprismatic S_8 geometry of the $Pt_2(p\text{-dtc})_4$.

The recent report by Browall, *et al.*,[34] of the structure of $M_2(S_2C_2H_2)_4$, M = Pd or Pt, further accentuates the need to consider the stereochemical arrangement of ligands in metal–metal bonded species. In the Browall compounds, where the M–M distances are 2.79 and 2.75 Å, respectively, a nearly cubic sulfur atom arrangement is found. The authors suggest that sulfur interactions contribute appreciably to the stabilization of these M_2S_8 structures.

While S–S interactions may indeed be important in controlling structures of "oxidized" sulfur–ligand systems such as the neutral 1,2-dithiolenes, other factors also must be involved. The "octahedral" NiS_6 geometry found[36] for $Ni[S_2CN(n\text{-Bu})_2]_3Br$ is a case in point, since strong S–S interactions might have been expected to produce a trigonal prismatic S_6 rhombus if this effect were dominant.[37]

In the case of the $Pt_2(p\text{-dtc})_4$ filled (and empty) $5d_{xy}$ and $5d_{x^2-y^2}$ orbitals on platinum atoms, Figure 6, can lead to a net δ bond formation and a minimization of d–d electron repulsion when one MS_4 unit is rotated 45° from its neighbor. Indeed, this is the structure commonly found for the columnar platinum(II) complexes. The structure of $Ni_2(S_2CCH_2C_6H_5)_4$ is similarly described.[38]

The observed antiprismatic M_2S_8 geometry in these formally d^8 metal complexes may be a result of combined effects including filled d orbital repulsions, nonbonding sulfur electron repulsions, and δ ($d_{x^2-y^2}$–d_{xy}) bond formation (at 2.87 Å d–δ orbital overlap is calculated to be very small). Crystallization forces also may be involved. The structure of $Mo_2(S_2COC_2H_5)_4$ reported recently by Ricard[39] to contain a 2.12 Å Mo–Mo distance and a nearly cubic sulfur atom geometry suggests, however, that sulfur–sulfur atom repulsions are not the sole determinants of structure in dithiolates. In the molybdenum compound an argument identical with that presented by Cotton and Harris[40] for the observed geometry of $Re_2Cl_8^{2-}$ and its quadrupole bond can be made to understand the structure.

If one assumes that stereochemical effects of the metal–metal interaction are important to a description of the structure of dimeric dithiolates, the contrasting geometries of the dimeric 1,2- and 1,1-dithiolates must be explained. A useful but clearly somewhat naive explanation may be made by ascribing a formal oxidation state of +4 to the metal atoms in the 1,2-dithiolates (dianionic ligands) and one of +2 to the metal atoms in the 1,1-dithiolates. In the latter complexes the filled d_{xy} (δ) orbitals on each metal center may lead to the antiprismatic twist observed, while with the empty metal δ orbitals in the 1,2-dithiolates, metal–metal interactions do not produce a stereochemical

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control of the geometry, and sulfur–sulfur bonding interactions may dominate the structure.

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14-Coordinate Uranium(IV). The Structure of Uranium Borohydride by Single-Crystal Neutron Diffraction[1]

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The structure of $U(BH_4)_4$ has been refined by a single-crystal neutron diffraction study. The X-ray structure (tetragonal, $P4_32_12$ ($P4_12_12$), $a = 7.49$ (1) Å, $c = 13.24$ (1) Å, $Z = 4$, $\rho_{calcd} = 2.66$ g/cm^3) has been confirmed and, in addition, all hydrogen atoms have been located to a precision of 0.04 Å. Four of the six BH_4^- ions surrounding each uranium atom are attached to it by two hydrogen atoms, and use their remaining two hydrogen atoms to bridge neighboring uranium atoms in a helical polymeric structure. Two additional tetrahydroborate groups in a cis configuration are bonded to the uranium atom by three hydrogen atoms, resulting in an overall coordination number of 14. The mean U–H bond length is 2.38 (2) Å. The BH_4^- ions are approximately tetrahedral with a mean B–H distance (corrected for thermal motion) of 1.29 (4) Å. A capped hexagonal antiprism is considered to be a useful reference coordination polyhedron, and distortions from this idealized geometry are described. The difference between the solid-state structures of $Zr(BH_4)_4$ and $U(BH_4)_4$ are discussed in terms of sphere packing and molecular orbital considerations. The results have also been used in conjunction with diffraction data on other metal tetrahydroborate compounds and with tabulated ionic radii to develop a single and consistent picture in which the metal–boron distance is shown to correlate with the geometry of the metal borohydride attachment.

Introduction

Knowledge of the molecular geometry of metal tetrahydroborate complexes is required for the interpretation of their physical and chemical properties. Of special interest is the mode of attachment of the BH_4^- group to the central metal ion, in particular, whether there are one, two, or three hydrogen atoms in the bridge bonds. To date, X-ray diffraction studies have established a two-point attachment for bis(tetrahydroborato)beryllium(II),[4] tetrahydroboratobis(triphenylphosphine)copper(I),[5] tris(tetrahydroborato)trimethylamine-aluminum(III),[6] and tetrahydroboratobis(h^5-cyclopentadienyl)titanium(III),[7] while electron diffraction results imply a similar bonding mode for tris(tetrahydroborato)aluminum(III).[8] Only tetrakis(tetrahydroborato)zirconium(IV) has been reported as having three hydrogen bridge bonds between the central transition metal atom and boron. This geometry has been suggested both by single-crystal X-ray diffraction[9] and gas-phase electron diffraction[10] studies.

The investigation of the crystal structure of uranium borohydride by X-ray[11] and neutron diffraction techniques was motivated by two basic considerations. First, knowledge of the geometry of the U–BH_4 attachment was desired in conjunction with the analysis of the spectroscopic properties of $M(BH_4)_4$ compounds, M = Zr, Hf, U, Th.[12] The need for sound structural data, in which the positions of all atoms are unambiguously located, is underscored by past difficulties with vibrational analyses of $M(BH_4)_4$ molecules.[13] For example, $Zr(BH_4)_4$ (12-coordinate, T_d symmetry, four BH_4^- groups having a three-point attachment)[9,10] and $U(BH_4)_4$ (14-coordinate, C_2 symmetry, four BH_4^- groups having a two-point and two BH_4^- groups having a three-point attachment, *vide infra*)[11] have been assumed on the basis of infrared data to be isostructural.[13,14] Thus, when dealing with such systems as $M(BH_4)_4$, knowledge of the molecular geometry is especially useful, perhaps even necessary, for the interpretation of vibrational data. Second, optical and electron paramagnetic resonance spectroscopic results on $U(BH_4)_4$ are now available[15] and their analysis depends in part on exact structural details.

A report of the single-crystal X-ray diffraction study of $U(BH_4)_4$ has already appeared.[11,16] The crystal

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