Table I. Dependence of Reciprocal Relaxation Times on Concentration and pH[a]

pH	τ^{-1}, sec^{-1}	$4(PFe(H_2O))Q/(H^+)^2$
6.09	0.76 ± 0.42	0.012
6.09	1.04 ± 0.12	0.082
6.59	1.48 ± 0.28	0.106
6.09	1.00 ± 0.32	0.220
6.42	1.27 ± 0.14	0.499
6.59	1.37 ± 0.07	0.639
7.05	1.37 ± 0.17	0.738
6.59	1.72 ± 0.1	1.408
6.72	1.68 ± 0.1	1.426
7.75	1.63 ± 0.5	1.75
7.36	1.59 ± 0.22	2.10
7.05	1.77 ± 0.13	2.83
7.09	2.22 ± 0.08	4.22
7.10	2.11 ± 0.1	4.72
7.05	2.09 ± 0.13	5.33
7.10	2.68 ± 0.44	7.07
7.10	2.42 ± 0.18	7.72
7.36	2.97 ± 0.21	12.03

[a] $Q = 2.5 \times 10^{-9}$ *M*, $T = 20°$, $\mu = 0.1$ *M*.

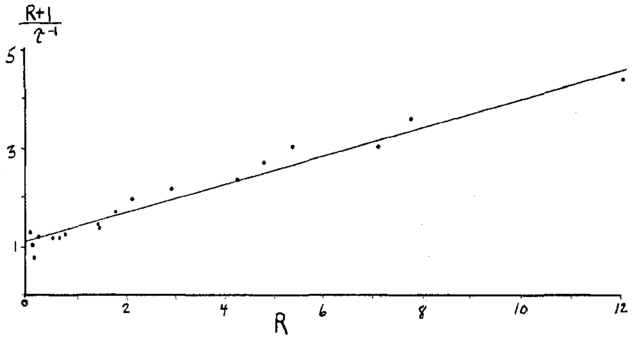

Figure 1. Plot of the kinetic data for the iron porphyrin monomer-dimer reaction at 20°.

usually attributed[11] to the reaction

$$\text{L-Fe(OH)}^- + \text{L-Fe(H}_2\text{O)} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(\text{L-Fe})_2\text{O}]^{2-} + \text{H}^+ + \text{H}_2\text{O} \qquad (9)$$

where the L represents various ligands coordinated to the ferric ion. We find no evidence of eq 9 making any contribution to the $FeTPPS_4$ kinetics in the pH range 5-7. The monomerization study was run below pH 3, where such a process could occur.

Our k_{-2} term for $Fe^{III}TPPS_4$ (0.9 sec^{-1} at 20°) is similar to those found for other iron complexes at 25°, for example,[11] EDTA (1.2 sec^{-1}), HEDTA (4.0), CyDTA (9.0), and H_2O (0.35). It has been suggested that the attacking nucleophile on such oxy-bridged dimers is a water molecule, which forms an unstable dihydroxy intermediate. Since it has been demonstrated that the Fe-$TPPS_4$ system, which shows no equilibrium evidence for $[PFe(OH)]^-$, goes through this species to form the dimer, systems in which there is definite evidence for $[PFe(OH)]^-$ (ENP, DPS_2, and TMTPyP) might behave in a similar fashion. Studies are underway to prove this point. Preliminary results indicate that five- or six-coordinated $TPPS_4$-metal complexes do not aggregate in aqueous solution, as found here with the pure monomer and dimer forms of $FeTPPS_4$. Many four-coordinate $TPPS_4$ metalloporphyrins dimerize.

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Registry No. $[\{(TPPS_4)Fe\}_2O]^{2-}$, 52486-65-4.

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Contribution from the Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60, 1QD, England

Palladium(II), Platinum(II), and Rhodium(III) Complexes of a Chelating Di(tertiary stibine), 1,3-Bis(diphenylstibino)propane. The Spectrochemical Position of a Distibine Ligand

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Very few coordination complexes of di(tertiary stibine) ligands have been reported[1] in contrast to the extensive studies of the phosphorus and arsenic analogs.[2,3] Bis(diphenylstibino)methane, $Ph_2SbCH_2SbPh_2$, behaves as a monodentate or bridging bidentate ligand[4] toward class B metals. Replacement of the methylene backbone by dimethylene or trimethylene should increase the tendency of the ligand to function as a chelating diantimony donor, and since all reported attempts to prepare 1,2-bis(diphenylstibino)ethane have failed,[5-7] we have investigated the palladium(II), platinum(II), and rhodium(III) complexes of 1,3-bis(diphenylstibino)propane. This forms part of a general investigation we are making of the donor properties of stibine ligands.[4,8]

Experimental Section

1,3-Bis(diphenylstibino)propane (dsbp) was prepared in ~50% yield by the reaction of sodium diphenylstibine and 1,3-dibromopropane in liquid ammonia.[9] *Anal.* Calcd for $C_{27}H_{26}Sb_2$: C, 54.5; H, 4.4. Found C, 54.2; H, 4.3; mp 54° (lit. value 52-53°[4]).

Pd(dsbp)Cl_2. Potassium tetrachloropalladate(II) (0.327 g, 1.0 mmol) and dsbp (0.594 g, 1.0 mmol) were stirred together under reflux in a 1:1 mixture of ethanol-dichloromethane for 1 hr, and the yellow product was filtered off, recrystallized from dichloromethane, and dried *in vacuo*. Yield ~75%.

Pd(dsbp)X_2 (X = Br, I, SCN) were obtained similarly in the presence of an excess of NaX. Yields 50-70%.

Pt(dsbp)X_2 (X = Cl, Br, I, SCN) were obtained from sodium tetrachloroplatinate(II), NaX, and dsbp in a water-ethanol-dichloromethane mixture under reflux for 2 hr. Recrystallization from dichloromethane yielded crystalline complexes in 50-70% yield.

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Table I. Analytical Data and Some Physical Properties of the Complexes

Compd	Color	Mp, °C	% C[a]	% H[a]	Ir data, cm^{-1}
$[Pd(dsbp)Cl_2]$[b]	Yellow	164	41.8 (42.0)	3.2 (3.4)	320, 295 ν(Pd–Cl)
$[Pd(dsbp)Br_2]$	Orange-brown	160	37.4 (37.8)	3.1 (3.0)	230, 205 ν(Pd–Br)
$[Pd(dsbp)I_2]$[c]	Purple	190	34.6 (35.3)	3.0 (2.6)	
$[Pd(dsbp)(SCN)_2]$[d]	Red	166	42.0 (42.6)	3.3 (3.1)	2105 sh, 2095 ν(CN)[e] 422 δ(NCS)
$[Pt(dsbp)Cl_2]$	Yellow	130	37.3 (37.6)	3.3 (3.0)	305, 283 ν(Pt–Cl)
$[Pt(dsbp)Br_2]$	Yellow	168	34.0 (34.1)	2.9 (2.7)	210 ν(Pt–Br)
$[Pt(dsbp)I_2]$	Yellow	185	30.7 (31.0)	2.7 (2.5)	
$[Pt(dsbp)(SCN)_2]$[f]	Yellow-green	178–180	37.9 (38.5)	3.0 (2.9)	2115 ν(CN),[g] 412 δ(NCS)
$[Rh(dsbp)_2Cl_2]Cl$	Orange	145–147	46.1 (46.3)	3.7 (3.7)	
$[Rh(dsbp)_2Br_2]Br$	Orange	150	42.0 (42.3)	3.4 (3.2)	
$[Rh(dsbp)_2I_2]I$	Red-black	205	38.9 (38.9)	3.3 (3.2)	

[a] Found (calculated). [b] Mol wt 762 (calcd 771). [c] Mol wt 927 (calcd 954). [d] % N, 3.2 (3.4). [e] CH_2Cl_2 soln, 2110 cm^{-1}. [f] % N, 3.0 (3.1). [g] CH_2Cl_2 soln, 2115 cm^{-1}.

Table II. Electronic Spectral Data

	E_{max} (ϵ_{mol})[a]		E_{max} (ϵ_{mol})[a]
$[Pd(dsbp)Cl_2]$	32.5 (14,590), 26.0 (7830)	$[Rh(dsbp)_2Cl_2]Cl$	27.0 (39,800)
$[Pd(dsbp)Br_2]$	31.8 (17,410), 24.5 (6580)	$[Rh(dsbp)_2Br_2]Br$	26.9 (36,600), ~24.0 sh
$[Pd(dsbp)I_2]$	31.1 (13,030), 21.9 (6020)	$[Rh(dsbp)_2I_2]I$[b]	26.7, ~23.0 sh
$[Pd(dsbp)(SCN)_2]$	29.8 (11,360), 23.4 (2840)		
$[Pt(dsbp)Cl_2]$	~31.0 sh (6600)	$[Pd(dpe)Cl_2]$[12]	28.9 (6570), 28.2 sh
$[Pt(dsbp)Br_2]$	30.0 (4380)	$[Pd(dpe)Br_2]$[12]	28.0 (6060)
$[Pt(dsbp)I_2]$	25.5 (6200)	$[Pd(dae)Cl_2]$[12]	27.2 (4450)
$[Pt(dsbp)(SCN)_2]$	~27.5 (2850)	$[Pd(dae)Br_2]$[12]	25.8 (4920)

[a] Dichloromethane solutions. [b] Only very slightly soluble.

$[Rh(dsbp)_2X_2]X$ (X = Cl, Br, I) were prepared from $RhX_3 \cdot 3H_2O$ and dsbp in a 1:2 ratio in an ethanol–dichloromethane mixture and recrystallized from dichloromethane. Yields ~80%.

Physical measurements were obtained as previously described.[4]

Results and Discussion

The reaction of 1,3-bis(diphenylstibino)propane (dsbp) with the appropriate MX_4^{2-} (M = Pd, Pt; X = Cl, Br, I, SCN) in a 1:1 molar ratio produced $M(dsbp)X_2$ complexes (Table I). These complexes are nonelectrolytes in 1,2-dichloroethane solution and the $[Pd(dsbp)X_2]$ (X = Cl, I) are monomeric in chloroform, indicating that the dsbp is functioning as a chelating ligand. The far infrared spectra of the chloro and bromo complexes also exhibit two ν(Pd-X) absorptions consistent with the necessarily cis structure. The infrared spectra of the $[Pd(dsbp)(SCN)_2]$ and $[Pt(dsbp)(SCN)_2]$ complexes in the solid state both exhibit the sharp ν(CN) frequencies (Table I) in the region expected for M-SCN bonding,[10] and in dichloromethane solution integrated intensity measurements[11] of the ν(CN) bands in $[Pd(dsbp)(SCN)_2]$ (2110 cm^{-1}, $\nu_{1/2} = 11$ cm^{-1}, $A = 2.03 \times 10^4$ cm^{-2} M^{-1}) and $[Pt(dsbp)(SCN)_2]$ (2115 cm^{-1}, $\nu_{1/2} = 13$ cm^{-1}, $A = 2.47 \times 10^4$ cm^{-2} M^{-1}) confirm that only M-SCN links are present. Moreover, the lowest energy electronic spectral bands move to lower energy in the order Cl > Br > SCN > I, as expected for a series of complexes which contain S-bonded thiocyanate groups.[12] The bis(triphenylstibine) analogs, $[M(SbPh_3)_2(SCN)_2]$, also contain S-bonded thiocyanates.[13]

Attempts to prepare $Pd(dsbp)_2X_2$ or $[Pd(dsbp)_2X]BPh_4$ in a pure state have been unsuccessful. The bulkiness of the dsbp ligands (terminal phenyl groups and a long trimethylene backbone) may preclude the formation of bisligand compounds for palladium(II), but if steric factors are operative then they are overcome by the tendency for rhodium(III) to have a CN > 4 because $[Rh(dsbp)_2X_2]X$ (X = Cl, Br, I) complexes are easily prepared. The chloro and bromo derivatives, $[Rh(dsbp)_2X_2]X$, are 1:1 electrolytes in 10^{-3} M solution in dichloroethane ($\Lambda_M = 24.5$ and 23.0 ohm^{-1} M^{-1} cm^2, respectively), but the iodo derivative was only slightly soluble in organic solvents.

Particular interest attaches to the spectrochemical position of dsbp, since electronic spectra of complexes containing chelating distibines have not previously been reported. Since the analogous complexes of 1,3-bis(diphenylarsino)propane have not been reported we have compared the distibine spectra with the corresponding compounds containing 1,2-bis(diphenylphosphino)ethane (dpe)[12] and 1,2-bis(diphenylarsino)ethane (dae).[12] These ligands differ from dsbp in having one fewer $-CH_2-$ group in the backbone which probably has a negligible effect on the spectra compared with differences due to changes in the group Vb donors. The relevant data are shown in Table II from which it can be seen that the donor set spectrochemical series is $P_2 > As_2 > Sb_2$, the same order found for monodentate group Vb donor ligands by Goggin, *et al.*[14] Similar comparisons are possible for the platinum series, although here the lowest energy bands in some cases appear as shoulders on the intense charge-transfer absorptions and thus accurate determination of the band maxima is difficult.

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Registry No. $[Pd(dsbp)Cl_2]$, 52393-05-2; $[Pd(dsbp)Br_2]$, 52393-06-3; $[Pd(dsbp)I_2]$, 52393-07-4; $[Pd(dsbp)(SCN)_2]$, 52393-08-5; $[Pt(dsbp)Cl_2]$, 52393-21-2; $[Pt(dsbp)Br_2]$, 52393-22-3; $[Pt(dsbp)I_2]$, 52393-23-4; $[Pt(dsbp)(SCN)_2]$, 52393-24-5; $[Rh(dsbp)_2Cl_2]Cl$, 52393-09-6; $[Rh(dsbp)_2Br_2]Br$, 52393-10-9; $[Rh(dsbp)_2I_2]I$, 52393-11-0.

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Preparation, Characterization, and Crystallographic Data of Some Substituted-Pyridinium Antimony(III) Bromide Salts[1,2]

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Structures of a wide variety of antimony(III) anions with fluoro and chloro ligands and differing in stoichiometry have been characterized, yet structures of only two involving bromo coordination, *viz.*, $SbBr_6^{3-}$ [5] and $Sb_2Br_9^{3-}$,[6] have been determined. Formation of other bromo-coordinated ions in the crystalline state, such as $SbBr_4^-$ or $SbBr_5^{2-}$ or their polymeric forms, should be possible. Indeed, by using 17 different aliphatic amines and three aromatic amines, Whealy and Yeakley[7] succeeded in synthesizing $R_xSb_yBr_z$ salts having R:Sb:Br ratios of 2:1:5, 3:1:6, and 3:2:7; all were yellow, varying only in shade. We decided to explore the synthesis of $R_xSb_yBr_z$ salts by considerably expanding the choice of aromatic amines, particularly in view of increasing structural evidence that (aromatic)N-*H*· · ·X (X = Cl or Br) hydrogen bonds are capable of inducing significant deformation of halogen-coordinated anions. We succeeded in synthesizing a variety of salts, some intensely colored, ranging from deep yellow to orange and red. R:Sb:Br ratios of 1:1:4, 2:1:5, and 3:2:9 were obtained. This note reports the preparation of these salts and some of their physical properties.

Experimental Section

Preparation. Each salt was prepared by allowing the appropriate amine to react with antimony tribromide in concentrated hydrobromic acid (48%). The antimony tribromide solution was first prepared by dissolving 0.0111 mol of reagent grade $SbBr_3$ in 10 ml of concentrated hydrobromic acid. To this was added an equimolar amount (0.0111 mol) of the amine. Liquid amines were added dropwise, with stirring, to the $SbBr_3$–HBr solution at room temperature. Reaction mixtures resulting from the addition of solid amines were heated to effect reaction. The amine:$SbBr_3$ ratio of 1:1 was arbitrarily used for initial syntheses, giving high yields only for those salts having R:Sb:Br of 1:1:4; yields were improved for the other salts when stoichiometric amounts of the starting materials were used.

The bromide salt of 1-methylpyridine, $C_6NH_8^+Br^-$, was used as the starting material for the 1-methylpyridinium derivative; it was added directly to the $SbBr_3$–HBr solution with heating. Preparation of the 1-bromopyridinium derivative made use of crystalline pyridinium bromide hydrobromide, $C_5NH_5Br^+Br^-\cdot HBr$, (from K & K Laboratories) as the starting material.[8] Direct addition of this orange-red solid to the $SbBr_3$–HBr solution at room temperature produced a black crystalline product. The mixture was heated to drive off molecular bromine and then allowed to cool, yielding this time light orange crystals.

Addition of pyridine, quinoline, isoquinoline, and the alkyl-substituted pyridines to $SbBr_3$ in HBr yielded crystalline precipitates on contact; these were filtered and recrystallized from hot concentrated hydrobromic acid. Reactions involving the halogenated pyridines (except that of 1-bromopyridine, as noted above) produced crystals only on standing, usually within 0.5 hr. Because it was believed that chemically pure $R_xSb_yBr_z$ salts formed in these latter cases, no recrystallizations were carried out. All 19 compounds, except the 2-fluoropyridinium derivative, crystallized as needles.

Physical and Crystallographic Measurements. The colors, melting points (in air), and observed densities (by flotation) are presented in Table I. Crystallographic unit cell data, also summarized in Table I, were determined using single-crystal Weissenberg and precession film techniques.

Empirical formulas for 17 of the 19 salts were derived by utilizing the relationship $d = ZM/N_0V$ (where d is the density, Z is the number of formula units of weight M per unit cell, N_0 is Avogadro's number, and V is the unit cell volume) in conjunction with elemental analysis[9] and fluorescence spectroscopy. Because Z is restricted to certain values by space group requirements, this expression proved to be quite sensitive and useful. In only two cases, formulas consistent with the crystal data could not be derived. Until all the salts are fully characterized by single-crystal structure determinations, it is appropriate to regard the empirical formulas in Table I as only tentative assignments.

Infrared Measurements. Infrared spectra of the 19 $R_xSb_yBr_z$ salts[10] were recorded with Perkin-Elmer Model 457 and 467 instruments. Samples were run as KBr pellets (3-mg sample in 300 mg of KBr). Several samples were examined as mulls in Nujol and Fluorolube for comparison with the KBr preparations. No appreciable shifts were noted and it is believed that no interaction between sample and KBr occurred. Wavelength calibration scans were made routinely of a polystyrene film.

Discussion

Two significant results emerged from this investigation. First, we have found that when aromatic amines are used as cations, R:Sb:Br ratios of 1:1:4, 2:1:5, and 3:2:9 can be obtained. Second, we have succeeded in identifying a variety of aromatic amines capable of forming antimony(III) bromide salts which are more deeply colored than those synthesized with nonaromatic cations. Whealy and Yeakley have noted that the 20 salts they synthesized were all yellow, varying only in shade. The pyridinium salt, $(C_5NH_6)_5Sb_2Br_{11}$, which contains the $Sb_2Br_9^{3-}$ ion, is also yellow,[6a] as are those with alkali cations. Table I shows that the most intensely colored salts contain the halogenated cations, notably the 1-bromo-, 2-fluoro-, 2-chloro, 2-bromo-, and 3,5-dichloropyridinium derivatives, which range in color

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(8) When recrystallized from concentrated hydrobromic acid, this compound has the following crystal data at room temperature: orthorhombic, space group *Pnma* or *Pna*2_1 with lattice parameters $a = 8.34$ (4), $b = 7.93$ (2), and $c = 13.67$ (4) Å.

(9) $R_xSb_yBr_z$ complexes of known composition were initially used to evaluate analytical methods available to us for determination of bromine (by titration with $AgNO_3$) and antimony (by wet oxidation with acid, reduction with SO_2, and titration with $KMnO_4$). Deviation of the measured from the calculated content averaged 3% for both elements. This deviation exceeded, by a factor of 1–3, the calculated range in Br and Sb content for $R_xSb_yBr_z$ salts having Sb:Br ratios 1:4, 1:4.5, and 1:5. Major sources of error were poor solubility of the salts in toluene–propanol–water mixtures for the bromine determinations and, in general, the presence of small amounts of hydrobromic acid adhering to the crystal surfaces. Accordingly, while reliable elemental analyses would have been desired for all 19 salts in this series, they were performed on only those for which empirical formulas derived by the other methods were inconclusive. No elemental analyses were performed for C or N content.

(10) See paragraph at end of paper regarding supplementary material.