Preparation of Some Thionitrosyl-type Transition-metal Complexes and Their Characterisation by Infrared, Optical, and Electron Paramagnetic Resonance Spectroscopy: [M(S_2N_2H)$_2$], [M(S_2N_2H)(S_3N)], and [M(S_3N)$_2$] (M = Co, Ni, Pd, or Pt)

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The title compounds have been prepared by revision of the literature methods. Improved yields of many of the compounds have been obtained, as well as isolation of the previously unobtainable [Pd(S_2N_2H)(S_3N)] and preparation of pure samples of [Pd(S_2N_2H)(S_3N)] and [Pt(S_3N)$_2$]. Infrared data are reported for the [M(S_2N_2H)(S_3N)] and [M(S_3N)$_2$] complexes and used to show that previous preparations for M = Pt have given impure products. The assignment of the spectra supports a *cis* square-planar geometry for all of the complexes reported. The optical absorption spectra of the complexes have been recorded, and show that the electronic transitions are mainly due to the ligands. Only the cobalt complexes give e.p.r. signals. Detailed studies of [Co(S_2N_2H)$_2$] at 10 K reveal the presence of a spin equilibrium between high- ($S = \frac{3}{2}$) and low-spin ($S = \frac{1}{2}$) cobalt(II).

TRANSITION-METAL thionitrosyl-type † complexes have been known for many years and compounds of the general types [M(S_2N_2H)$_2$], [M(S_2N_2H)(S_3N)], and [M(S_3N)$_2$] have been reported for nickel,[1-3] cobalt,[2,4] iron,[5] palladium,[4,6] and platinum.[6] The preparative methods described in the literature, apart from being complicated, tend to be directed towards specific complexes and in addition problems have been encountered in some of the preparations.[7] A general preparative technique, applicable to a wide range of metals and which yields all three types of complex, is clearly required. This paper describes such a method, which is based upon the early work of Daum *et al.*[2] Improved yields of many of the previously prepared complexes have been obtained and, in addition, the previously unobtainable [Pd(S_2N_2H)(S_3N)] has been isolated and pure samples of [Pt(S_2N_2H)(S_3N)] and [Pt(S_3N)$_2$] have been obtained.

The i.r. spectra of the [M(S_2N_2H)(S_3N)] and [M(S_3N)$_2$] complexes lend support to our recent assignments of the spectra of the [M(S_2N_2H)$_2$] complexes.[8] The spectra of the platinum complexes are of additional interest since they show differences from the spectra of the same compounds reported by Haworth and Lin.[9] We propose that these differences, which manifest themselves as extra bands in the earlier spectra, are due to impurities in the samples. The assignment of the i.r. spectra of the [M(S_2N_2H)(S_3N)] and [M(S_3N)$_2$] complexes, taken together with our recent assignment of the spectra of the [M(S_2N_2H)$_2$] series, provides confirmation for the previously assumed *cis* square-planar geometry for all of the thionitrosyl-type complexes under consideration here.

Having developed new preparative and purification procedures for the complexes, we have investigated their electronic structures. Several workers have discussed the bonding in simple sulphur–nitrogen compounds.[10-13] However, little work has been reported on the electronic structures of metal complexes with S–N ligands. *X*-Ray photoelectron spectroscopy has established clearly the oxidation state of the metal as II in complexes of the type [M(S_2N_2H)$_2$] (M = Co, Ni, Pd, or Pt).[14] It is to be expected that the Pd^{II} and Pt^{II} will be diamagnetic, low-spin d^8 ions, with the magnetic states of the Ni^{II} and Co^{II} species being uncertain. Therefore, we have carried out an e.p.r. study of these species and also recorded the u.v. and the visible absorption spectra of the complete series of metal complexes.

EXPERIMENTAL

Infrared spectra, in the region 200—4 000 cm^{-1}, were recorded using Perkin-Elmer 557 and 577 instruments; the samples were presented as pressed alkali-metal halide discs (B.D.H. Spec. grade KBr or CsI). A Beckman IR720M instrument was employed for the far-i.r. region (50—60 cm^{-1}), the samples being measured as Nujol mulls on Polythene plates.

All chemicals were of laboratory grade unless stated otherwise. Methanol was dried by refluxing over Mg–I_2 followed by distillation. Tetrahydrofuran was dried by distillation from Li[AlH_4]. Benzene and carbon tetrachloride were dried over 4A molecular sieves. Tetrasulphur tetranitride (S_4N_4) was prepared by the standard method,[15] and freshly recrystallised from toluene before use. Anhydrous $NiCl_2$ and $CoCl_2$ were prepared by refluxing the hydrated metal chloride with freshly distilled thionyl chloride.[11]

T.l.c. plates were prepared using Merck Kieselgel 60 PF_{254} (Art 7747). A suspension of Kieselgel (40 g) in water (110 cm^3) was spread evenly over a glass plate (12 × 37 cm). After drying in air for 24 h, the plates were activated by heating to 85 °C in an oven for a minimum of 24 h.

Absorption spectra were recorded on a Cary 14 spectrophotometer, e.p.r. spectra with a Varian E-3 spectrometer working in the *X*-band region, and variable-temperature e.p.r. spectra using a type E.S.R.-9 helium-flow cryostat (Oxford Instruments Ltd.). The e.p.r. spectra were obtained as the first derivative of the absorption and the *g* values quoted were taken at peak maxima for absorption-shaped bands and at the cross-over point for derivative-shaped bands. Absorption spectra were recorded in B.D.H.

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† These complexes have also been termed thiazenes or dithiazenes. The I.U.P.A.C. requirements are not satisfied by either of these names. Indeed, there seems to be no simple systematic name for these complexes.

spectroscopic grade solvents, whilst e.p.r. spectra were obtained using AnalaR solvents.

In general it was found that the pure complexes were stable as solids, but decomposed in solution within a few days. The complexes were stored *in vacuo* in the dark. The basic preparative approach for the thionitrosyl-type complexes follows the early work of Daum *et al.*[2] who prepared [Ni(S_2N_2H)$_2$] and [Co(S_2N_2H)$_2$] by the reaction of the appropriate metal chloride with S_4N_4 in methanol. However, since several of the complexes are only formed in low yield, great importance attaches to the working-up procedure, and we found that preparative thin-layer chromatography (p.t.l.c.) is extremely useful for this purpose. This technique was preferred over column chromatography because of the ease with which small quantities can be handled and its speed, which was especially important on account of the instability of some of the complexes in solution. One other important advantage of p.t.l.c. is its economy with respect to solvents and absorbent relative to column chromatography.

Moreover, use of p.t.l.c. made it possible to take advantage of the conversion (1) in a very convenient way. We

$$2[\mathrm{M(S_2N_2H)(S_3N)}] \longrightarrow [\mathrm{M(S_2N_2H)_2}] + [\mathrm{M(S_3N)_2}] \qquad (1)$$

found that this procedure can be adopted successfully with p.t.l.c. plates to give easily obtainable samples of [M(S_3N)$_2$] (M = Ni, Co, or Pt). Indeed, for platinum this was the only method to give pure [Pt(S_3N)$_2$].

In view of the similarity of the preparations for the various metals only those for nickel are described in detail, although any substantial differences are noted for specific complexes.

Nickel Complexes.—Tetrasulphur tetranitride (10 g, 54 mmol) was ground,* and added to anhydrous $NiCl_2$ (12 g, 92 mmol) and dried methanol (800 cm^3). This mixture was refluxed under nitrogen for 6 h, during which time it became deep violet. After cooling, the solution was decanted and evaporated to dryness under reduced pressure. The resulting solid was washed with water on a sintered glass funnel until the water was free of Cl^-, and extracted with a minimum quantity of dry tetrahydrofuran (thf) (typically 5 × 15 cm^3). This solution was placed on p.t.l.c. plates and eluted with benzene. The mixture separated into three bands: violet, R_F 0.2, due to [Ni(S_2N_2H)$_2$]; red, R_F 0.87, due to [Ni(S_2N_2H)(S_3N)] and S_4N_4; and green, R_F 0.95, due to [Ni(S_3N)$_2$] and sulphur (a full set of R_F values is given in Table 1).

[Ni(S_2N_2H)$_2$]. This was obtained by extracting the violet band from p.t.l.c. with acetone, placing this solution on p.t.l.c. plates, and eluting once again with benzene. Extraction of the resulting violet band gave, after pumping away the solvent, pure [Ni(S_2N_2H)$_2$] as dark black needles (6.6 g, 49.5%) (Found: H, 1.05; N, 22.8; Ni, 24.0; S, 51.8. Calc. for $H_2N_4NiS_4$: H, 0.80; N, 22.85; Ni, 24.0; S, 52.35%).

[Ni(S_2N_2H)(S_3N)]. This was obtained by extracting the red band from p.t.l.c. with benzene, and chromatographing the resulting material a second time with carbon tetrachloride. The S_4N_4 preceded the [Ni(S_2N_2H)(S_3N)] up the plate. After extracting the resulting red band from the silica gel using benzene and pumping off the solvent, pure red [Ni(S_2N_2H)(S_3N)] remained (0.47 g, 3.5%) (Found: H, 0.35; N, 16.15; S, 61.45. Calc. for HN_3NiS_5: H, 0.40; N, 16.05; S, 61.15%).

[Ni(S_3N)$_2$]. This was obtained from the green p.t.l.c. band by repeatedly chromatographing using either n-pentane or cyclohexane to remove sulphur. This yielded 4 mg of product. However, it was more convenient to make use of the conversion described in equation (1). Thus a solution of [Ni(S_2N_2H)(S_3N)] (40 mg) in benzene was placed on one p.t.l.c. plate and left for 72 h in the dark before elution using CCl_4. The resulting p.t.l.c. had components due to all three nickel complexes, with [Ni(S_3N)$_2$] well separated from the other two. The [Ni(S_3N)$_2$] was extracted using n-pentane. After pumping away the solvent, pure [Ni(S_3N)$_2$] remained as a dark red solid (8 mg) which gave green solutions (Found: N, 10.2; S, 69.1. Calc. for N_2NiS_6: N, 10.05; S, 68.95%).

TABLE 1

R_F values of compounds eluted with benzene, carbon tetrachloride, and cyclohexane

Compound	Colour of solution	Eluant		
		C_6H_6	CCl_4	C_6H_{12}
[Ni(S_2N_2H)$_2$]	Violet	0.19	0.0	0.02
[Ni(S_2N_2H)(S_3N)]	Red	0.87	0.35	0.05
[Ni(S_3N)$_2$]	Green	0.95	0.99	0.72
[Co(S_2N_2H)$_2$]	Violet	0.91	0.0	0.02
[Co(S_2N_2H)(S_3N)]	Green	0.89	0.35	0.05
[Co(S_3N)$_2$]	Green	0.95	0.99	0.73
[Pd(S_2N_2H)$_2$]	Red	0.14	0.0	0.0
[Pd(S_2N_2H)(S_3N)]	Green	0.85	0.34	0.05
[Pd(S_3N)$_2$]	Blue	0.94	0.96	0.67
PdS_4N_2	Red	0.92	0.94	0.61
[Pt(S_2N_2H)$_2$]	Blue	0.15	0.0	0.02
[Pt(S_2N_2H)(S_3N)]	Red	0.85	0.35	0.05
[Pt(S_3N)$_2$]	Green	0.94	0.98	0.74
S_4N_4	Orange	0.85	0.65	0.30
S_8	Yellow	0.95	0.94	0.74

Cobalt Complexes.—Tetrasulphur tetranitride (9 g, 49 mmol) and anhydrous $CoCl_2$ (10 g, 77 mmol) were refluxed in dried methanol (500 cm^3) for 1.5 h under nitrogen. The resulting deep violet mixture was treated in the same way as the nickel preparation.

[Co(S_2N_2H)$_2$]. This was obtained as dark black crystals (2.8 g, 23%) which gave deep violet solutions (Found: H, 1.15; Co, 23.5; N, 22.55. Calc. for $H_2CoN_4S_4$: H, 0.80; Co, 24.0; N, 22.85%). Sulphur analyses gave poor results because of metal interference. The metal was determined using atomic absorption.

[Co(S_2N_2H)(S_3N)]. This was obtained as a dark black solid (0.37 g, 2.8%) that gave green solutions (Found: H, 0.45; Co, 23.0; N, 16.4. Calc. for $HCoN_3S_5$: H, 0.40; Co, 22.45; N, 16.0%).

[Co(S_3N)$_2$]. It was almost impossible to separate this complex from sulphur and so it was usually prepared from [Co(S_2N_2H)(S_3N)] as previously outlined for nickel, except that the solution was only left on the plate for 30 min before elution (Found: Co, 20.5; N, 10.1. Calc. for CoN_2S_6: Co, 21.1; N, 10.05%).

Palladium Complexes.—It has been reported that the addition of water to the reaction mixture in the palladium preparation affects the yields of the various complexes.[4] We have found that the water present in laboratory grade methanol was sufficient to aid the formation of [Pd(S_3N)$_2$], whilst if rigorous drying procedures were adopted the yield of [Pd(S_2N_2H)$_2$] was very low, even in the presence of pyridine. We were able to improve the yields of all the

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* **CAUTION**: S_4N_4 is explosive; it was ground moistened with a little methanol.

complexes by the addition of ammonium chloride as an aid to dissolution of the $PdCl_2$.

Tetrasulphur tetranitride (14 g, 76 mmol), $PdCl_2$ (10 g, 56 mmol), and $[NH_4]Cl$ (5 g, 95 mmol) were refluxed in laboratory grade methanol (650 cm³), under nitrogen, for 3 h. The resulting deep red mixture was treated in the same way as the nickel preparation.

$[Pd(S_2N_2H)_2]$. This was obtained as a red-brown amorphous powder after purification using p.t.l.c. The quality of the product was improved by recrystallisation from cyclohexane–dioxan (1 : 1), with slow addition of cyclohexane. The resulting deep red needles were dried *in vacuo* at 70 °C, to yield 3.8 g (26%) (Found: H, 0.90; N, 19.1; S, 44.05. Calc. for $H_2N_4PdS_4$: H, 0.70; N, 19.15; S, 43.8%).

$[Pd(S_2N_2H)(S_3N)]$. This was obtained, in the same way as the corresponding nickel complex, as a dark black solid (0.6 g, 3.4%) which gave green solutions (Found: H, 0.65; N, 13.8; S, 51.5. Calc. for HN_3PdS_5: H, 0.30; N, 13.55; S, 51.75%). This is the first time this complex has been isolated. Weiss and Thewalt [4] reported that it decomposed on work up.

$[Pd(S_3N)_2]$. This was obtained directly in relatively large amounts, by taking the blue band from the first p.t.l.c. of the palladium reaction mixture and chromatographing with cyclohexane. This yielded 65 mg of the blue compound (Found: N, 8.10; S, 58.95. Calc. for N_2PdS_6: N, 8.60; S, 58.8%).

A further red complex was obtained in low yield (5 mg) during the purification of $[Pd(S_3N)_2]$. This compound has a slightly lower R_F than $[Pd(S_3N)_2]$, and is presumably the compound that Weiss and Thewalt suggested was PdS_4N_2. We were unable to obtain reproducible analyses for this compound because of rapid decomposition. However, its i.r. spectrum has bands which indicate similar S–N units to those seen in $[Pd(S_2N_2H)_2]$ and $[Pd(S_3N)_2]$, but does not contain any bands due to N–H. The spectrum is certainly not identical to that of any of the other palladium complexes, and comparison with our other i.r. data seems to indicate a structure containing at least four different S–N bonds.

Platinum Complexes.—Several methods were investigated for the preparation of the platinum complexes. The reported procedure of reaction of H_2PtCl_6 with S_4N_4 in dimethylformamide (dmf) gave reasonable results, but is fraught with difficulties, not the least being complete removal of the dmf from the products. The complexes could also be obtained by reaction of $PtCl_2$ with S_4N_4 in refluxing methanol, but only in low yields. This method lacked reproducibility because of the varying quality of commercial $PtCl_2$. The most convenient method was found to be the reaction of $Na_2[PtCl_6]$ with S_4N_4 in the presence of sodium dithionite. Thus, S_4N_4 (4.1 g, 22 mmol), $Na_2[PtCl_6]$ (10 g, 22 mmol), and $Na_2[S_2O_4]$ (3.8 g, 22 mmol) were refluxed together in methanol (650 cm³) for 3 h. The deep blue reaction mixture was treated in the same way as the nickel preparation.

$[Pt(S_2N_2H)_2]$. This was obtained in a similar way to the palladium complex as blue needles after recrystallisation (1.1 g, 15%) (Found: H, 0.55; N, 14.1; S, 33.15. Calc. for $H_2N_4PtS_4$: H, 0.55; N, 14.7; S, 33.65%).

$[Pt(S_2N_2H)(S_3N)]$. This was obtained in the same way as the nickel complex as a dark red solid (0.95 g, 11.5%) which gave red solutions (Found: H, 0.55; N, 10.4; S, 39.9. Calc. for HN_3PtS_5: H, 0.25; N, 10.55; S, 40.25%). Haworth and Lin [9] reported a strong band in the i.r. at 800 cm⁻¹ for this complex. We did not observe this band for any of $[M(S_2N_2H)(S_3N)]$ complexes.

$[Pt(S_3N)_2]$. This could not be obtained directly from the reaction mixture in a pure state. Even after several chromatographs the complex could not be freed of an impurity which was seen on microscopic examination as clear crystals. The i.r. spectrum of this impure material contained bands due to the pure compound and additional bands which Haworth and Lin reported at 600 and 455 cm⁻¹.

A pure sample could be obtained by the conversion [*cf.* equation (1)] of $[Pt(S_2N_2H)(S_3N)]$ on p.t.l.c. plates. Thus, a solution of $[Pt(S_2N_2H)(S_3N)]$ (200 mg) in benzene was placed on p.t.l.c. plates and eluted immediately with CCl_4. The $[Pt(S_3N)_2]$ was extracted from the p.t.l.c. plate as quickly as possible using n-pentane. After pumping away the solvent, 3 mg of the pure complex remained (Found: N, 6.55; Pt, 47.5. Calc. for N_2PtS_6: N, 6.75; Pt, 46.95%). The low yield from the conversion indicates the instability of the complex. If, as in the nickel and cobalt conversions, the $[Pt(S_2N_2H)(S_3N)]$ was left on the p.t.l.c. plate for any length of time before elution, rather than improving the yield, this resulted in the presence of the impurity already mentioned.

The i.r. spectrum of this complex is similar to those observed for the equivalent complexes with the other metals. It does not contain the previously reported [9] bands at 800 and 455 cm⁻¹.

Our data indicate that we have successfully prepared pure samples of $[Pt(S_2N_2H)(S_3N)]$ and $[Pt(S_3N)_2]$ and suggest that the previously reported i.r. data are in error as a result of impurities.

RESULTS AND DISCUSSION

(1) *Infrared Spectra.*—The i.r. spectra of the $[M(S_3N)_2]$ and $[M(S_2N_2H)(S_3N)]$ (M = Co, Ni, Pd, or Pt) complexes are shown in Figures 1 and 2; the data are also tabulated (Tables 2 and 3). Of the above compounds, the only one for which an *X*-ray structure determination is available is $[Pd(S_3N)_2]$ which has the *cis* square-planar geometry. The similarity of the i.r. spectra of these materials shows that all the $[M(S_3N)_2]$ complexes have this structure. Comparison of the present spectra with those of the corresponding $[M(S_2N_2H)_2]$ species recently reported [8] confirms that the *cis* square-planar geometry is normal for compounds of all three types, $[M(S_2N_2H)_2]$, $[M(S_2N_2H)(S_3N)]$, and $[M(S_3N)_2]$. This is an important result since the

TABLE 2

Infrared spectra (cm⁻¹) of $[M(S_3N)_2]$ complexes

Co	Ni	Pd	Pt	Assignment
948m	986m	1 007m	1 001 (sh)	$\nu(S^3-N^2)$
			994m	
718 (sh)	725s	702s	710 (sh)	$\nu(S^1-N^2)$
704s	711s	692s	700s	
526 (sh)	529w	516 (sh)	525mw	$\nu(S-S)$
521mw	519m	511m	514m	
508mw	500mw	490 (sh)	492w	ring def.
496w	486w	479mw	480w	
	385vw			
375mw	352vw	374vw		$\nu(M-S^1)$
327mw	322m	319mw	329mw	$\nu(M-S^1)$
318m	303mw	301mw	311w	ring def.
277w	265mw	246mw	239w	$\nu(M-S^3)$

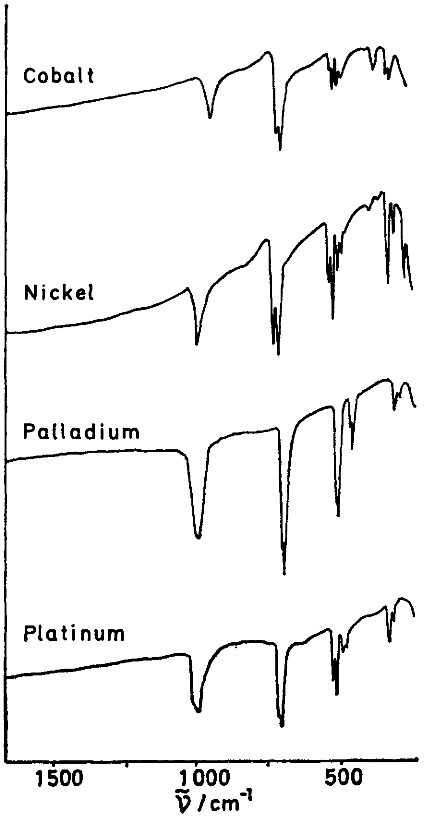

FIGURE 1 Infrared spectra of $[M(S_3N)_2]$ complexes

widely assumed *cis* square-planar geometry for all these compounds appears to rest solely upon the *X*-ray analysis of the compounds shown in Figure 3.

The $[M(S_3N)_2]$ compounds are related to the $[M(S_2N_2H)_2]$ complexes by the substitution of an NH group by sulphur. This has a marked effect on the spectra. The vibrations due to the NH group and the $\nu(S^2–N^1)$ vibration disappear. The $\nu(S^2–N^2)$ vibration occurs at lower frequency than in $[M(S_2N_2H)_2]$, whilst the $\nu(S^1–N^2)$ vibration is unaffected.

TABLE 3

Infrared spectra (cm^{-1}) of $[M(S_2N_2H)(S_3N)]$ complexes. Primed atoms belong to the S_3N ring

Co	Ni	Pd	Pt	Assignment
3 160m,br	3 160m,br	3 185m,br	3 180m,br	ν(N–H)
1 245w,br	1 220mw	1 198w,br	1 245w,br	δ(N–H)
1 225w,br		1 172w,br	1 202w,br	δ(N–H)
1 014 (sh)	1 045 (sh)	1 069 (sh)	1 041ms	$\nu(S^2–N^2)$
1 006m	1 036m	1 060ms		
936 (sh)	969 (sh)	990 (sh)	982 (sh)	$\nu(S^{2\prime}–N^{2\prime})$
928m	961m	983m	970m	
854m	885m	891mw	876ms	$\nu(S^2–N^1)$
721s	722 (sh)	716s	714vs	$\nu(S^1–N^2)$
		708s		
708s	709s	698s	700vs	
675vw,br	625m,br	631w	645w	
	600w,br	604w	618w	δ(N–H)
527w				
515s	523s	521s	522s	$\nu(S'–S')$
495w	501w	496vw	491w	ring def.
471w	463w	435vvw	486vw	ν(M–N)
405vw	391w	392w	400vw	ring def. + ν(M–S)
383m	362vw	374vw	378w	ν(M–S)
338s	327s	318s	325s	ν(M–S)
323m	317 (sh)	315 (sh)	317 (sh)	ring def.
308w	303w	302 (sh)	310 (sh)	
295m	294s	272m	263mw	$\nu(M–S')$
278w				ring def.
264w	248w		234w	
208w	203mw	226vw	198vw	

The $\nu(S^3–S^2)$ vibration appears in the region of 450—530 cm^{-1} for all of the $[M(S_3N)_2]$ complexes, but assignment is complicated by the presence of a group of four bands. Since they occur in pairs the higher-frequency set are assigned as the $\nu(S^3–S^2)$ vibration split by coupling through the metal. The lower-frequency pair are assigned to a ring deformation likewise split by coupling.

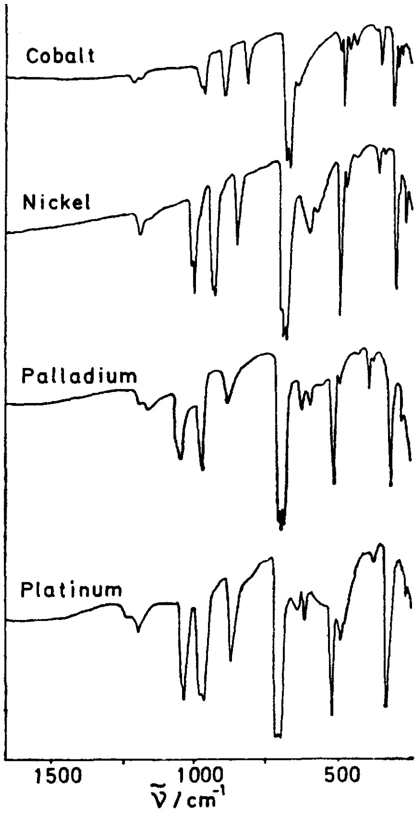

FIGURE 2 Infrared spectra of $[M(S_2N_2H)(S_3N)]$ complexes

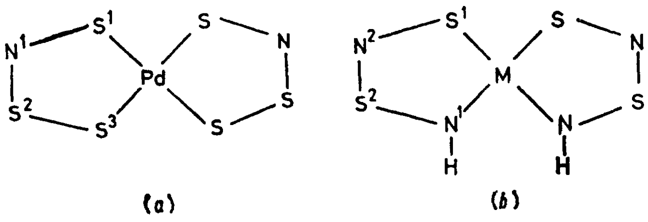

FIGURE 3 (*a*) Structure of $[Pd(S_3N)_2]$ according to Weiss and Neubert (*Z. Naturforsch.*, 1966, **B21**, 287); (*b*) structure of $[M(S_2N_2H)_2]$ complexes (M = Co, Ni, Pd, or Pt)

In the low-frequency region bands will arise due to the $\nu(M–S^1)$ vibration; however, they will change in frequency only slightly on going from $[M(S_2N_2H)_2]$ to $[M(S_3N)_2]$. For example, the ν(Ni–S) vibrations at 357 and 332 cm^{-1} in $[Ni(S_2N_2H)_2]$ occur at 352 and 322 cm^{-1} respectively in the spectrum of [Ni(S$_3$N)$_2$]. Assignment of the rest of the far-i.r. spectrum presents rather greater difficulties. Two ν(M–S^3) vibrations are expected, although one of them may be weak.

The spectra of the [M(S$_2$N$_2$H)(S$_3$N)] complexes (Figure 2, Table 3) are found to be, in general, the sum of the spectra of the [M(S$_2$N$_2$H)$_2$] and [M(S$_3$N)$_2$] complexes. One of the ν(N–H) vibrations and two of the δ(N–H) seen for the [M(S$_2$N$_2$H)$_2$] complexes have disappeared as expected since, with only one NH group, in- and out-of-phase contributions are no longer possible. In the region around 500 cm^{-1} the spectra are rather simpler for these complexes than for [M(S$_3$N)$_2$]. This confirms that the complexity of the spectra in the last case is a result of the coupling of vibrations through the metal. This cannot occur here because the two rings have different vibrational frequencies which therefore interact only weakly.

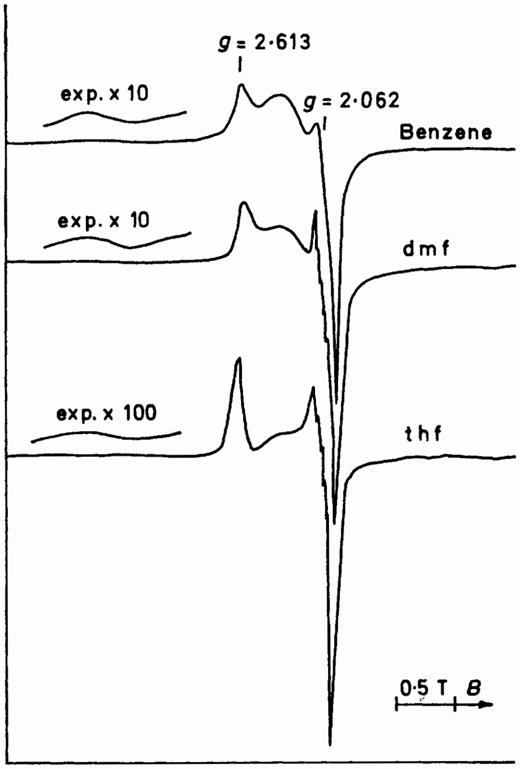

Figure 4 E.p.r. spectra of [Co(S$_2$N$_2$H)$_2$] in various solvents. Operating conditions: 10 K, microwave power 20 mW, microwave frequency 9.236 GHz; modulation amplitude 27 mT (benzene), 6.3 mT (dmf, thf); receiver gain 4 × 10^3 (benzene), 4 × 10^2 (dmf, thf solution)

(2) *E.P.R. Spectra*.—No e.p.r. signals could be obtained at room temperature from any of the nickel, palladium, or platinum complexes, or at 77 K from the nickel complexes. However, the cobalt complexes give readily observable signals in solution so a thorough investigation was carried out on these compounds. E.p.r. spectra of the pure solid cobalt compounds are too broad to be of value, but spectra at room temperature and at 10 K have been obtained for [Co(S$_2$N$_2$H)$_2$] in the solvents dmf, dimethyl sulphoxide (dmso), thf, and benzene (Figure 4, Table 4). The room-temperature spectra show one symmetric band with g = 2.17, but the low-temperature spectra are more complex and solvent dependent. The solvent dependence of the band intensities suggests that there are two species giving rise to e.p.r. signals. The bands with g = 5.32 and 2.16 vary in intensity with solvent far more than those with g = 2.61 and 2.06. In order to confirm that the two sets of signals arise from different species the dependence of the spectrum upon microwave power was examined (Figure 5). The bands at g = 5.32 and 2.16 increase with increasing microwave power, whereas the other signals are apparently independent of the power used. The different power dependence of the intensities of the

TABLE 4

g values from e.p.r. spectra of cobalt thionitrosyl-type complexes

Compound	Solvent	T/K	g
[Co(S$_2$N$_2$H)$_2$]	thf	297	2.175
	thf	10	2.06, 2.61, 5.32
	dmso	10	2.06, 2.16, 2.61, 5.32
	dmf	10	2.06, 2.16, 2.61, 5.32
	Benzene	10	2.06, 2.16, 2.61, 5.32
[Co(S$_2$N$_2$H)(S$_3$N)]	thf	297	2.17
	thf	10	2.06, 2.61, 5.33
[Co(S$_3$N)$_2$]	Benzene	297	2.17
	Benzene	10	2.04, 2.16, 2.58, 5.33

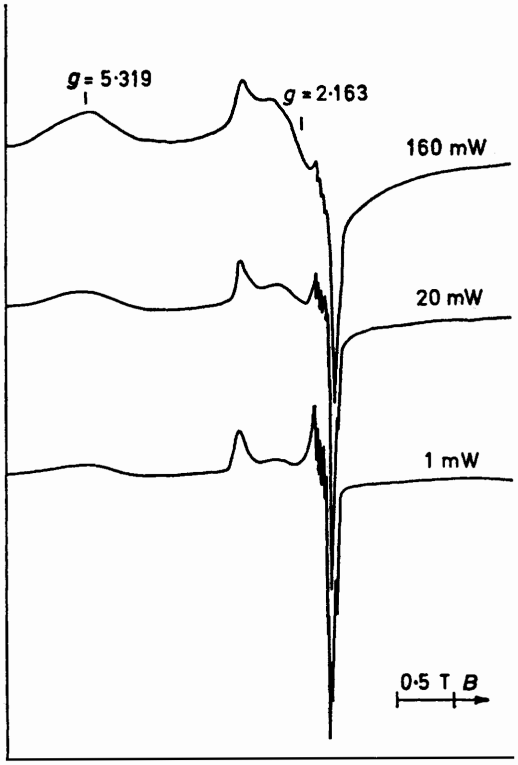

FIGURE 5 E.p.r. spectra of [Co(S$_2$N$_2$H)$_2$] in dmso at various microwave powers. Operating conditions: 10 K, modulation amplitude 6.3 mT, microwave frequency 9.236 GHz; receiver gain 5 × 10^3 (upper, middle), 10 × 10^3 (lower spectrum)

two sets of signals shows quite clearly that two paramagnetic species are present at 10 K.

The signal at $g = 2.06$ has well resolved hyperfine structure (Figure 6) with eight peaks separated by 27 mT. This confirms the origin of the band as a cobalt species, the hyperfine structure arising from ^{59}Co ($I_n = \frac{7}{2}$). The g values of 2.06 and 2.61 are assigned to low-spin Co^{II} in a planar environment, being comparable with previously reported values for low-spin planar Co^{II}, *e.g.* cobalt myoglobin[16] (2.33 and 2.02) and [NBu$_4$]$_2$-[Co{S$_2$C$_2$(CN)$_4$}$_2$][17] (2.798, 2.025, and 1.977).

Neither of the weaker bands shows any nuclear hyperfine structure, so an unambiguous assignment to a cobalt-containing species cannot be made. However, a careful check of the e.p.r. (at 10 K) of the solvents used revealed no trace of these signals, which were also observed in two different preparative batches of the complexes. The large departure of the signals from the spin-only value also eliminates the possibility that the signals are due to radicals. In the light of the above evidence, these bands may be assigned to the cobalt complex with a reasonable degree of certainty.

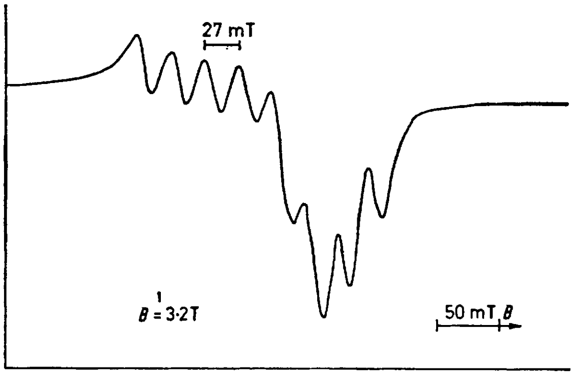

FIGURE 6 E.p.r. spectrum of [Co(S$_2$N$_2$H)$_2$] showing expansion of band with $g = 2.062$ and hyperfine coupling. Operating conditions: dmso solution; 10 K; microwave power 1 mW; modulation amplitude 6.3 mT; receiver gain 8 × 10^3; microwave frequency 9.236 GHz

High-spin cobalt(II) (d^7) gives rise to e.p.r. signals characteristic of a paramagnet with $S = \frac{3}{2}$. Although e.p.r. studies of high-spin cobalt(II) complexes are not numerous, examples can be found of this ion in a range of co-ordination geometries. For example, in a planar environment, high-spin cobalt(II) myoglobin, the g values are 3.87 and 1.7;[16] in a distorted tetrahedral site, CoCl$_2$(py)$_2$ (py = pyridine), the values are 6.085, 2.677, and 1.790;[18] whereas in an octahedral site, Co[NH$_4$]$_2$[SO$_4$]$_2$·6H$_2$O, the values are 6.45 and 3.06.[19] This brief survey shows that observed g factors alone cannot be used as indicators of the co-ordination geometry of the high-spin cobalt(II) ion. However, we can conclude that the signals reported here for [Co(S$_2$N$_2$H)$_2$] at $g = 5.32$ and 2.6 should be assigned to the high-spin ($S = \frac{3}{2}$) form of cobalt(II). Also it is shown that a solvent-dependent spin equilibrium is present in solutions of [Co(S$_2$N$_2$H)$_2$] at 10 K. Qualitatively, the equilibrium appears to be pushed towards the high-spin form by changing solvents in the order benzene > dmf > dmso > thf as expected if the solvent is binding to the fifth and sixth axial positions of a planar complex. The existence of a similar spin equilibrium at room temperature has not, of course, been established by this work. Attempts to use the strong-field ligand pyridine as a solvent to abolish the high-spin signals were unsuccessful because of decomposition of the complex by pyridine.

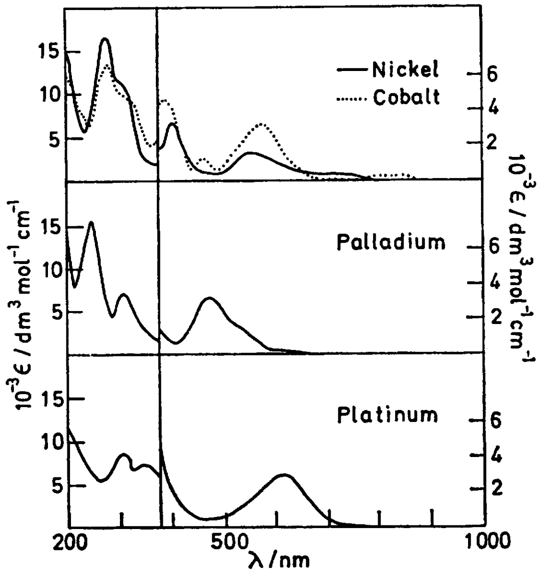

FIGURE 7 Optical absorption spectra of [M(S$_2$N$_2$H)$_2$] complexes

(3) *Optical Absorption Spectra.*—The electronic spectra of the thionitrosyl-type complexes are illustrated in Figures 7—9. The [M(S$_2$N$_2$H)$_2$] and [M(S$_2$N$_2$H)(S$_3$N)] complexes were examined in ethanolic solutions and the [M(S$_3$N)$_2$] in cyclohexane. The spectra of several of the

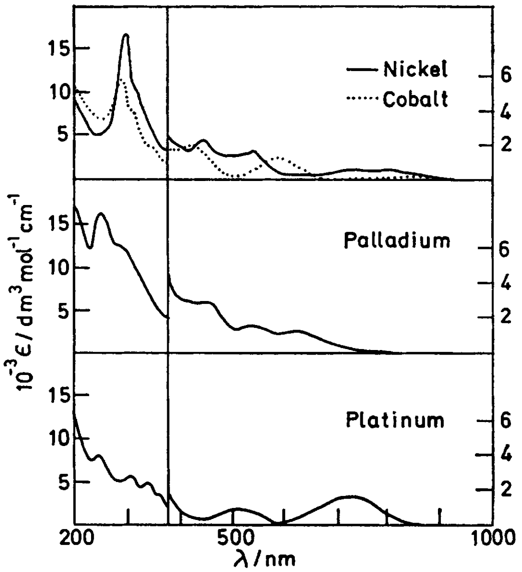

FIGURE 8 Optical absorption spectra of [M(S$_2$N$_2$H)(S$_3$N)] complexes

complexes were studied in a variety of solvents, namely benzene, thf, n-pentane, and ethanol. No change in the wavelengths of the absorption maxima were seen with the variation in solvent. The high absorption coefficients of the bands suggest that the transitions responsible arise from ligand-localised electrons and are not due to *d*–*d* or M–L transitions. This testifies to the presence of low-lying ligand orbitals. CNDO calculations on the uncomplexed $S_2N_2H^-$ ligand support this argument by indicating the presence of unfilled π* orbitals of low energy.[20] The transitions observed may thus arise from π–π* transitions of the pseudo-aromatic ligands.

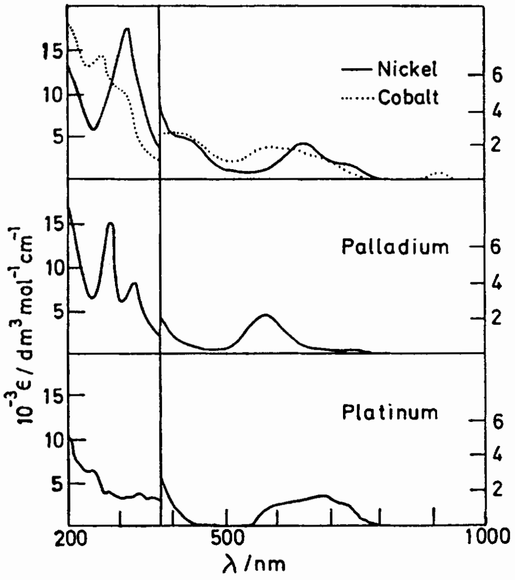

FIGURE 9 Optical absorption spectra of $[M(S_3N)_2]$ complexes

The spectra of the $[M(S_3N)_2]$ complexes are broadly similar to those of $[M(S_2N_2H)_2]$ for a given metal ion. In the high-energy region (200—400 nm) only small shifts of the bands are apparent. At longer wavelengths (400—800 nm) the spectra still give bands with a one-to-one correspondence, although the visible bands move to lower energy on changing the ligand from $S_2N_2H^-$ to S_3N^-.

As expected, the spectra of the mixed-ligand complexes, $[M(S_2N_2H)(S_3N)]$, are more complicated than the others, but do contain, apparently, a superposition of the bands seen in the spectra of the other two types of complexes. Only the cobalt complexes show weak low-energy transitions, *i.e.* at 1 280 nm for $[Co(S_2N_2H)_2]$ and at 1 260 nm for $[Co(S_2N_2H)(S_3N)]$, but the absorption coefficients of these bands are very low. Since the bands are absent from the spectra of the complexes of the nickel, palladium, and platinum complexes, they are almost certainly *d*–*d* in origin.

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