817. *Infrared Spectra and Structure of Some Simple and Bridged Nitro-complexes of Platinum, Palladium, and Cobalt.*

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The infrared spectra of some dinitro-complexes of platinum(II), palladium(II), and cobalt(III) have been examined. The spectra of the *trans*-isomers have bands (some of which are split) in the regions around 1415 (v_3), 1330 (v_1), and 822 cm.$^{-1}$ (v_2). The *cis*-isomers have somewhat similar spectra with v_1 shifted to rather lower frequency and the characteristic addition of a band at about 1350 cm.$^{-1}$; also v_2, which is a single band in the spectra of the *trans*-isomers, is sharply split in the spectra of the *cis*-isomers. Two binuclear complexes having bridging nitro-groups were also examined. Their spectra have bands due to bridging nitro-groups near 1480 and 1200 cm.$^{-1}$. From these we infer that the nitro-group forms bridges through the nitrogen and one oxygen atom as hitherto assumed, *viz.*, M–N(O)–O–M. The spectra of a number of mononitro- and polynitro-complexes are also recorded.

Beattie and Tyrrell [1] examined some nitroammine complexes of tervalent cobalt in the infrared region between 4000 and 700 cm.$^{-1}$ using the potassium bromide disc technique; it was concluded that the geometrical isomers of the dinitrotetramminecobalt(III) complex may be distinguished by examination of the spectra in the 1300 and 850 cm.$^{-1}$ regions. Nakamoto *et al.*[2] have also interpreted the splitting of the cobalt–ammonia stretching frequencies in various nitroammines in a similar manner. It had been suggested earlier [3] that the spectrum of the *cis*-dinitrotetramminecobalt(III) cation, $[Co^{III}(NO_2)_2(NH_3)_4]X$ where X = a singly charged anion, should show more bands than the *trans*-isomer, owing to the lower symmetry. An extra band was observed for the *cis*-isomer in the 1350 cm.$^{-1}$ region.

The present work was undertaken to ascertain whether there were features in the infrared spectra which could be used to distinguish between *cis*- and *trans*-isomers of planar complexes, and if possible to assign absorption bands characteristic of bridging nitro-groups. The variation of NO_2 stretching frequencies with different electronic effects transmitted through the metal atom was also investigated.

Results and Discussion.—The frequencies of the NO_2 absorption bands of the compounds examined are given in Tables 1—4.

¹ Beattie and Tyrrell, *J.*, 1956, 2849.
² Nakamoto, Fujita, and Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.
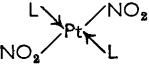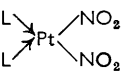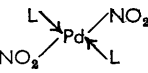³ Faust and Quagliano, *J. Amer. Chem. Soc.*, 1954, **76**, 5346.

The most recent assignment of the absorption frequencies for the non-linear triatomic NO_2^- group, which belongs to the point group C_{2v}, are given below together with the vibration type.[4] All three fundamental frequencies are active in the infrared region of the spectrum. These vibration types also occur when the NO_2 group is co-ordinated to a metal atom as the local symmetry of the group remains the same.

Type	No.	ν (cm.$^{-1}$)	Assignment
A_1	ν_1	1328 ± 2	Symm. stretch
A_1	ν_2	$828 \cdot 2 \pm 0 \cdot 4$	NO_2 bend
B_1	ν_3	1261 ± 3	As. stretch

The above assignment of ν_1 and ν_3 is incorrect because the asymmetric vibration always has the higher of the stretching frequencies. This has been assumed in our assignment of bands in the spectra of the complexes. Table 1 gives the NO_2 frequencies of a series of platinous and palladous nitro-complexes *cis-* and *trans*-$[L_2Pt(NO_2)_2]$ and *trans*-$[L_2Pd(NO_2)_2]$ containing a variety of uncharged ligands (L), examined in chloroform solution. The bending frequencies were obtained from acetone solutions. The ligands include, *e.g.*, amines, di-n-butyl sulphide, tri-n-butylphosphine, and tri-n-butylarsine.

The symmetric stretching modes of $NO_2(\nu_1)$ produce sharp bands in the range 1340—1318 cm.$^{-1}$, whereas the asymmetric stretching modes (ν_3) cause broader absorption bands, often with several shoulders, the principal maxima of which lie in the range 1440—1390 cm.$^{-1}$. The strongest band in the 1400 cm.$^{-1}$ region is considered to be the asymmetric NO_2 stretching band. The *cis*-isomers have, in addition, a third fairly broad band in the region 1355—1337 cm.$^{-1}$. This almost certainly is due to the lower symmetry of the *cis*-than of the *trans*-compounds, and would arise from the out-of-phase symmetric vibration of the two NO_2 groups. An alternative explanation, that it arises from steric interactions of the neighbouring NO_2 groups whereby one of the NO_2 groups is twisted out of the plane of the complex, as has been postulated to account for the splitting of the nitro-group frequencies in *o*-dinitroaryl compounds,[5] is very unlikely. With the greater angle between the nitro-groups in the complexes, their steric interaction will be very small indeed.

TABLE 1. NO_2 *absorption frequencies (cm.$^{-1}$) of some platinous and palladous complexes.*

	L	pepy *	PBu$^n_3$	AsBu$^n_3$	Bu$^n_2$S	Pr$^n_2$Se	Pr$^n_2$Te
(L₂Pt, trans)	as.	1412 b	1394 b	1401 b	1419 b	1423 sh / 1409 b	1418 sh / 1400 b
	sym.	1337	1328	1328	1333	1331	1326
	bend	822	819	—	820 s / 822 w.sh	—	—
(L₂Pt, cis)	as.		1418 sh / 1401 / 1382 sh / 1337 b		1432 b / 1416 sh / 1347 b		
	sym.		1323 sh		1322		
	bend		817 } 798		825 } 818		
(L₂Pd, trans)	as.	1411 b	1412 sh † / 1396 b	1400 b	1426 sh † / 1413 b	1426 sh / 1410 b	1420 sh / 1401 b
	sym.	1332	1327	1324	1327	1325	1321

* pepy = 4-n-pentylpyridine; s = strong; w = weak; sh = shoulder; b = broad.
† The splittings were observed by using a grating instrument.

In the 800 cm.$^{-1}$ region, examined in acetone, ν_2 appears as a single sharp band in the range 822—819 cm.$^{-1}$ for the *trans*-isomers, whereas the *cis*-isomers have two sharp and

[4] Weston and Brodasky, *J. Chem. Phys.*, 1957, **27**, 683.
[5] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958, p. 301.

quite distinct bands in the ranges 825—817 cm.⁻¹ and 818—798 cm.⁻¹. The double peak arises because in the *cis*-compound both the in-phase and the out-of-phase vibration are infrared-active. This splitting in the case of the *cis*-isomers and the presence of an additional band in the 1350 cm.⁻¹ region are considered to be characteristic of these isomers on the basis of the above compounds and the bisethylenediaminecobalt(III) complexes to be described here.

It is immediately apparent that no simple relation exists between the values of the NO_2 stretching frequencies, within the above defined ranges, and the type of donor atom in the uncharged ligands. In the *trans*-platinous or -palladous complexes the highest values of the asymmetric frequencies occur when di-n-butyl sulphide is the uncharged ligand (L), and the lowest frequencies when tri-n-butylphosphine is the donor group. On the other hand, the highest symmetric NO_2 frequencies occur when L is an amine, and the lowest when L is di-n-propyl telluride.

The factors affecting the NO_2 stretching frequencies in these compounds are obviously complicated, and the frequencies alone do not lend themselves to any obvious interpretation in terms of electronic effects transmitted through the metal atoms from the ligands (L). However, the fact that the frequencies do not follow a sequence parallel to that of the electronegativities of the donor atoms in L implies that something other than the inductive effects of the ligands is transmitted across the metal atoms to the nitro-groups. One such an effect could be caused by d_π-bonding between donor atoms with vacant d-orbitals of suitable energy in the ligand L, and the metal atom.

Bisethylenediaminecobalt(III) *complexes.* A series of mononitro-complexes of bisethylenediaminecobalt(III) was first examined, and by comparison with the spectrum of trisethylenediaminecobalt(III) chloride, and other complexes not containing nitro-groups, the frequencies listed in Table 2 were deduced for the nitro-groups. From this series of

TABLE 2. *Nitro-group frequencies (cm.⁻¹) of complexes of the type* [Co(en)₂(NO₂)Y]X.

	trans-*Isomers*				cis-*Isomers*			
Y	X	ν_3	ν_1	ν_2	Y	X	ν_3	ν_1	ν_2
SCN	SCN	1418 s	1318 s	825 s	Cl	NO₂	1404 s	1323, 1312 s	826 s
SCN	Cl	1413 s	1326 s	822 s	SCN	Cl	1416 s	1318 s	819 s
SCN	NO₂	1410 s	1326 s	820 s	SCN	NO₂	1416 s	1323 s	819 s
Cl	SCN	1427 s	1335 s	824 s	Cl	Cl	1401 s	1319 s	825 s

en = ethylenediamine; s = strong.

mononitro-complexes, it is apparent that there is little variation in frequency when the nitro-group is *cis*- or *trans*- to the other anionic ligands present. The frequency ranges observed were: ν_3, 1414 ± 13; ν_1, 1323 ± 12; ν_2, 822 ± 4 cm.⁻¹.

TABLE 3. *Nitro-group frequencies (cm.⁻¹) of complexes of the type* [Co(en)₂(NO₂)₂]X.

X	trans-*Isomers*			cis-Isomers			
	ν_3	ν_1	ν_2	ν_3		ν_1	ν_2
NO₃	1433 s	1348 sh / 1319 s	828 s	1425 s / 1404 s	1344 s	1314 s	830 s / 821 s
NO₂	1435 s	1335 s / 1318 s	823 s	1418 s / 1404 s	1348 s	1314 s	828 s / 821 s
I	1418 / 1404 s	1321 s / 1305 s	816 s	—	—	—	—
Cl	1414 s	1325 s / 1312 sh	819 s	1422 s / 1397 sh	1344 s	1323 wsh / 1312 s / 1304 wsh	832 s / 819 s
SCN	1422 s	1332 s / 1314 sh	824 s	1416 s / 1395 sh	1344 s	1316 s	827 s / 821 s

In Table 3 are listed the frequencies of the nitro-groups in the *cis*- and *trans*-isomers of a series of dinitrobisethylenediaminecobalt(III) complexes. The *trans*-isomers of the

dinitro-series have bands with the following ranges: ν_3, 1419 ± 16; ν_1, 1334 ± 14 and 1312 ± 7; ν_2, 822 ± 6 cm.$^{-1}$. The *cis*-isomers of the dinitro-series have bands with the ranges: ν_3, 1420 ± 5 and 1399 ± 5; ν_1, 1314 ± 2; ν_2, 829 ± 3 and 820 ± 1 cm.$^{-1}$. There is an additional band at 1346 ± 2 cm.$^{-1}$.

In the spectra of the *trans*-dinitro-complexes only one band was observed corresponding to ν_3, whereas in the case of the *cis*-isomers this band is split. The frequencies assigned to ν_3 and ν_2 for the *trans*-isomers were very similar to those obtained for the mononitro-complexes. ν_1 was split in the *trans*- but not in the *cis*-isomers. However, an extra band was observed in the spectra of the *cis*-isomers at about 1350 cm.$^{-1}$; this was reported [2] for the *cis*-dinitrotetramminecobalt(III) anion where it was stated to be a natural consequence of the lower symmetry.

The band arising from the bending vibration (ν_2) was split into two distinct peaks in the *cis*-dinitro-isomers with frequency ranges of 829 ± 3 and 820 ± 1 cm.$^{-1}$, as in the *cis*-platinous complexes previously described.

This splitting of ν_2 when two nitro-groups are in *cis*-positions to one another was also observed for the compounds given below:

$Na_2[Pd(NO_2)_4]$	848 s	825 s
$Na_2[RuNO(NO_2)_4OH],2H_2O$	837 vs	829 vs

Mathieu [6] examined the Raman spectra of two tetranitro- and two hexanitro-complexes of Group VIII metals and reported bands at 846 ± 1 and 833 ± 2 cm.$^{-1}$ for each of these compounds. The 827 cm.$^{-1}$ band of sodium nitropalladate falls outside this range, but this compound decomposed while being examined. The frequencies reported are listed below:

$Na_2[Pt(NO_2)_4]$	1412	1364	1325	847	835
$Na_2[Pd(NO_2)_4]$	—	—	—	—	827 *
$Na_3[Rh(NO_2)_6]$	1406	1380	1322	847	832
$Na_3[Ir(NO_2)_6]$	1408	1370	1327	846	835

<div align="center">* Decomposed during measurement.</div>

Bands appear in the regions expected for ν_3 and ν_1, and an extra band appears at 1372 ± 8 cm.$^{-1}$ as observed here for the *cis*-dinitro-isomers.

It appears therefore that, whenever two nitro-groups are in *cis*-relation to one another and attached to the same central metal atom, the band in the 820 cm.$^{-1}$ region is split and an extra band occurs in the 1350 cm.$^{-1}$ region. Sometimes one of the two bands observed here for ν_2 may be infrared-inactive; *e.g.*, only one peak is observed at 845 cm.$^{-1}$ in the spectrum of $Na_3[Co(NO_2)_6]$.

Complexes containing bridging nitro-groups. Infrared spectroscopy has been very valuable in establishing the existence of carbonyl (CO) [7] and thiocyanate (SCN) [8] bridging groups in metal co-ordination complexes. A few examples are known where the nitro-group functions as a bridging group between metal atoms, and we have examined two of these, *viz.*, dinitrobis(tri-n-butylphosphine)-$\mu\mu'$-dinitropalladium(II) (I) and bistetrammine-μ-nitro-μ-aminocobalt(III) chloride (II).

In Table 4 are given the frequencies of the absorption bands in the spectra of $[(PBu^n_3)_2Pd(NO_2)_2]$ and of the bridged complexes of palladium (chloro-, nitro-, and oxalato-bridges) in carbon tetrachloride and of cobalt(III) (nitro- and amido-, and peroxy- and amido-bridges) in potassium bromide discs.

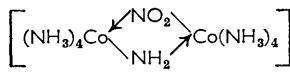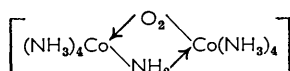[6] Mathieu, *J. Chim. phys.*, 1939, **36**, 271, 308.
[7] Sheline and Pitzer, *J. Amer. Chem. Soc.*, 1950, **72**, 1107.
[8] Chatt and Duncanson, *Nature*, 1956, **176**, 997; *J.*, 1958, 43.

The spectrum of the nitro-bridged palladium complex was measured in carbon tetra-chloride solution in the sample beam, with the corresponding chloro-bridged complex in the reference beam of the double-beam spectrometer, thereby reducing the apparent absorption due to alkyl groups. The nitro-bridged complex was also run in opposition to the corresponding *trans*-dinitro-mononuclear complex to ascertain whether there was any absorption arising

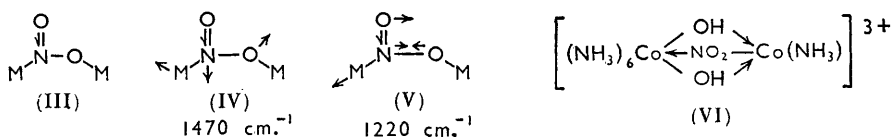TABLE 4. NO_2 *Frequencies* $(cm.^{-1})$ *of some bridged complexes.*

Compound	Bridged NO_2	NO_2	NO_2	Bridged NO_2
$(PBu^n_3)_2Pd_2(NO_2)_4$	1475 s	1421 s	1330 s	1238 s
$(PBu^n_3)_2Pd_2(C_2O_4)(NO_2)_2$		1429 s	1326 s	
$(AsBu^n_3)_2Pd_2Cl_2(NO_2)_2$		1421 s	1322 s	
$(PBu^n_3)_2Pd(NO_2)_2(trans)$		1414 sh *	1326 s	
		1395 b		

	Bridged NO_2	NH_3/NH_2	NH_3/NH_2	Bridged NO_2
$\left[(NH_3)_4Co \overset{NO_2}{\underset{NH_2}{\diagup\diagdown}} Co(NH_3)_4 \right] Cl_4, H_2O$	1485	1340	1296	1183
$\left[(NH_3)_4Co \overset{O_2}{\underset{NH_2}{\diagup\diagdown}} Co(NH_3)_4 \right] Cl_4, 4H_2O$		1332	1298	

* The splittings were observed by using a grating instrument

from the bridged nitro-group which was obscured by the terminal nitro-absorption bands. The asymmetric NO_2 stretching frequency of the mononuclear complex does not exactly cancel owing to a splitting of this band not present in the binuclear complex. No additional absorption was observed for the binuclear complex. By comparison with the spectrum of the corresponding mononuclear complex of palladium, it is clear that the bridged group is giving rise to absorption bands at 1472 ± 3 and 1230 ± 10 cm.$^{-1}$, the limits covering the use of different solvents (CCl_4 and $CHCl_3$).

The cobalt complexes showed absorption assigned to the nitro-bridging group at 1485 and 1183 cm.$^{-1}$, these being determined by comparison with the corresponding peroxy-bridged complex. It is noteworthy that no absorption characteristic of the peroxy-bridge was observed. The difference between the frequencies observed for the cobalt and the palladium complexes may be ascribed either to the use of potassium bromide discs, or to the fact that the cobalt complexes contain a five-membered ring system compared with the six-membered system in the palladium complexes.

In the esters of carboxylic acids absorption bands in the 1700 and 1200 cm.$^{-1}$ regions have been assigned to the stretching vibrations of the CO bonds, and by analogy we suggest that the structure of the bridging nitro-group has the form (III), the frequencies observed arising from the vibrations (IV) and (V). If the nitrogen atom alone were in the bridge then the NO_2 stretching frequencies would be expected to lie closer together. In agreement with this, Nakamoto, Fujita, and Murata [2] have recently assigned bands at 1516 cm.$^{-1}$ and 1200 cm.$^{-1}$ in the spectrum of the ion (VI) to vibrations of the bridging nitro-group. They also propose the same structure as we do for the bridging nitro-group.

EXPERIMENTAL

Determination of Spectra.—The infrared spectra were obtained with Grubb–Parsons double-beam or single-beam infrared spectrometers equipped with S3A monochromators and rock-salt

prisms. The mulling agents used were Nujol (2–15 μ) and hexachlorobutadiene. The latter was used for the region obscured by Nujol absorption bands. Solvents used were chloroform and carbon tetrachloride (1500—1200 cm.$^{-1}$) and acetone (830—800 cm.$^{-1}$).

The solid samples, with the exception of the bridged cobalt complexes which were examined in potassium bromide discs, were examined between rock-salt plates; in cases where it appeared likely that replacement of NO_2 by chloride from the rock-salt would occur, the plates used were coated with a fine film of polystyrene.[9]

Preparation of Compounds.—The nitro-complexes were prepared by established methods, and their configurations established by measuring their $\Delta\varepsilon/f$,[10] where $\Delta\varepsilon$ = the increment in dielectric constant due to the substance in dilute benzene solution and f = the mole-fraction of the substance. The products are colourless unless otherwise stated.

trans-*Dinitro-(4-n-pentylpyridine)platinum.* The dichloro-analogue [11] (2 g.) and sodium nitrite (2 g.) in methanol (75 c.c.) were boiled under reflux for 4 hr. The almost colourless solution was evaporated to dryness, and the *product* washed with water, dried, and recrystallised from ethanol, to give plates, m. p. 163—163·5°, $\Delta\varepsilon/f$ = 4·5 (yield 82%) (Found: C, 41·3; H, 5·5; N, 9·7. $C_{20}H_{30}O_4N_4Pt$ requires C, 41·0; H, 5·2; N, 9·6%).

trans-*Dinitrobis(tri-n-butylphosphine)platinum.* Potassium chloroplatinite (2·1 g.) and sodium nitrite (2 g.) in water (50 c.c.) were shaken until the solution became pale yellow. Tri-n-butylphosphine (2·0 g.) was then added in a nitrogen atmosphere, and the mixture shaken for 20 hr. The resulting white precipitate was removed and dried. Three recrystallisations from aqueous methanol gave the *product* as prisms, m. p. 147·5—148·5°, $\Delta\varepsilon/f$ = 3·4 (yield 51%) (Found: C, 41·9; H, 8·1; N, 3·9. $C_{24}H_{54}O_4N_2P_2Pt$ requires C, 41·7; H, 7·9; N, 4·0%).

trans-*Dinitrobis(tri-n-butylarsine)platinum* was similarly prepared and twice recrystallised from aqueous ethanol to give plates, m. p. 102·5—103° (yield 46%), $\Delta\varepsilon/f$ = 3·5 (Found: C, 37·0; H, 7·3; N, 3·5. $C_{24}H_{54}O_4N_2As_2Pt$ requires C, 37·0; H, 7·0; N, 3·6%).

trans-*Dinitrobis(di-n-butyl sulphide)platinum.* Hydrated sodium chloroplatinite (2 g.) in methanol (25 c.c.) was added to sodium nitrite (1·2 g.) in methanol (50 c.c.), and the solution kept until it had turned yellow. Di-n-butyl sulphide (1·7 c.c.) was then added. After 24 hr. this solution was evaporated to dryness; the residual *product* (12%), recrystallised from methanol, decomposed at 194·5—196° and had $\Delta\varepsilon/f$ = 12·1 (Found: C, 33·4; H, 6·5; N, 4·4. $C_{16}H_{36}O_4N_2S_2Pt$ requires C, 33·15; H, 6·3; N, 4·8%).

trans-*Dinitrobis(di-n-propyl selenide)platinum* was prepared in the same way as its tri-n-butylphosphine analogue but with only 4 hours' shaking and recrystallisation from methanol; it had m. p. 173—174° (sinters 170°) (yield 63%), $\Delta\varepsilon/f$ = 13·2 (Found: C, 23·6; H, 4·6; N, 4·4. $C_{12}H_{28}O_4N_2PtSe_2$ requires C, 23·3; H, 4·6; N, 4·5%).

trans-*Dinitrobis(di-n-propyl telluride)platinum* was prepared similarly. The pale orange product on extraction with hot light petroleum (b. p. 60—80°) gave a solution which on cooling deposited pale yellow needles, m. p. 46—47° (41%) (Found: C, 20·3; H, 4·0; N, 4·3. $C_{12}H_{28}O_4N_2PtTe_2$ requires C, 20·2; H, 3·95; N, 3·9%).

cis-Dinitrobis(tri-n-butylphosphine)platinum was prepared through the corresponding sulphate in a manner similar to that by which Jensen [12] prepared its ethyl analogue.

Sulphatobis(tri-n-butylphosphine)platinum. The dichloro-analogue (2 g.) and silver sulphate (10 g., 10 equiv.) were shaken in methanol (75 c.c.) for 20 hr. The mixture was filtered, and the filtrate taken to dryness. The residue on repeated recrystallisation from ethyl acetate gave the *complex* as needles (0·9 g.), m. p. 175—176·5° (Found: C, 41·2; H, 7·8. $C_{24}H_{54}O_4SP_2Pt$ requires C, 41·4; H, 7·8%).

cis-*Dinitrobis(tri-n-butylphosphine)platinum.* The sulphato-compound (0·7 g.) in methanol (20 c.c.) was treated with sodium nitrite (0·3 g.) in water (4 c.c.), and the mixture boiled under reflux for 15 min., then filtered. The residue was extracted with methanol (10 c.c.), and the combined filtrates were evaporated to dryness. The residue, twice recrystallised from methanol, gave pale cream leaflets (0·6 g.), m. p. 140·5—142°, $\Delta\varepsilon/f$ = 280 (Found: C, 41·9; H, 8·0; N, 4·0%).

cis-Dinitrobis(di-n-butyl sulphide)platinum, prepared as described by Löndahl [13] from

[9] Gatehouse, *Chem. and Ind.*, 1957, 1351.
[10] Chatt and Wilkins, *J.*, 1953, 70.
[11] Ahrland and Chatt, *J.*, 1957, 1379.
[12] Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.
[13] Löndahl, see Gmelin, "Handbuch der Anorganischen Chemie," Platinum, Part D, System No. 68, p. 318.

$(Bu^n{}_2S)_2PtSO_4$ and crystallised from aqueous ethanol, had m. p. 199° (decomp.) (softened over a wide range) (Löndahl gave m. p. 193°), $\Delta\varepsilon/f = 147\cdot0$ (Found: C, 33·0; H, 6·5; N, 4·8%).

trans-*Dinitrobis-(4-n-pentylpyridine)palladium.* Hydrated sodium chloropalladite (3 g.) and sodium nitrite (3 g.) in methanol (*ca.* 75 c.c.) were treated with 4-n-pentylpyridine (3 c.c.). The mixture was taken to dryness at 100°, and the residue extracted with water, leaving a yellow residual *complex* which recrystallised from acetone as yellow plates, m. p. 131—132·5° (74%), $\Delta\varepsilon/f = 5\cdot6$ (Found: C, 48·5; H, 6·1. $C_{20}H_{30}O_4N_4Pd$ requires C, 48·3; H, 6·1%).

trans-Dinitrobis(tri-n-butylphosphine)palladium,[12] obtained analogously to Mann and Purdie's preparation of its n-propyl homologue,[14] had m. p. 141—142°, $\Delta\varepsilon/f = 3\cdot5$ (Found: Pd, 17·6; C, 47·7; H, 9·0; N, 4·4. Calc. for $C_{24}H_{54}O_4N_2P_2Pd$: Pd, 17·7; C, 47·8; H, 9·0; N, 4·65%).

trans-Dinitrobis(tri-n-butylarsine)palladium,[12] similarly prepared, had m. p. 96°, $\Delta\varepsilon/f = 3\cdot7$ (Found: Pd, 15·4; C, 42·0, 41·55; H, 7·8. Calc. for $C_{24}H_{54}O_4N_2As_2Pd$: Pd, 15·4; C, 41·7; H, 7·9%).

trans-Dinitrobis(di-n-butyl sulphide)palladium,[15] prepared in similar manner to its platinum analogue, had m. p. 171—172°, $\Delta\varepsilon/f = 9\cdot3$ (Found: Pd, 21·7; C, 39·0; H, 7·35; N, 5·5. Calc. for $C_{16}H_{36}O_4N_2S_2Pd$: Pd, 21·7; C, 39·1; H, 7·4; N, 5·5%).

trans-*Dinitrobis(di-n-propyl selenide)palladium* was prepared in the same way as its platinum analogue and recrystallised from methanol as yellow leaflets, m. p. 145—146° (gradual softening) (72%), $\Delta\varepsilon/f = 10\cdot7$ (Found: C, 27·3; H, 4·9; N, 5·6. $C_{12}H_{28}O_4N_2PdSe_2$ requires C, 27·3; H, 5·3; N, 5·3%).

trans-*Dinitrobis(di-n-propyltelluride)palladium* was similarly prepared from potassium chloropalladite (2·3 g.), potassium nitrite (3 g.), and di-n-propyl telluride (4 g.). The reddish product (4·9 g.) was extracted with boiling light petroleum (b. p. 60—80°) (200 c.c.), and the filtrate, on cooling, deposited orange needles, m. p. 58—59° (with premature softening) (1·5 g.) (Found: C, 23·1; H, 4·5; N, 4·55. $C_{12}H_{28}O_4N_2PdTe_2$ requires C, 23·0; H, 4·5; N, 4·5%).

Dinitrobis(tri-n-butylphosphine)-$\mu\mu'$-dinitrodipalladium [14] had m. p. 138° (Found: Pd, 26·2; C, 35·7; H, 6·9; N, 7·1. Calc. for $C_{24}H_{54}O_8N_4P_2Pd_2$: Pd, 26·6; C, 35·9; H, 6·8; N, 7·0%). Dinitrobis(tri-n-butylphosphine)-μ-oxalatopalladium [14] had m. p. 200—205° (decomp.) (Found: Pd, 26·65; C, 39·0; H, 6·8. Calc. for $C_{26}H_{54}O_8N_2P_2Pd_2$: Pd, 26·7; C, 39·1; H, 6·8%).

Dinitrobis(tri-n-butylarsine)-$\mu\mu'$-dichlorodipalladium was prepared following Mann and Wells's directions [16] but by using $Bu^n{}_3As$ in place of Me_3As; it had m. p. 124° (Found: Pd, 24·2; C, 32·8; H, 6·15. $C_{24}H_{54}O_4N_2Cl_2As_2Pd_2$ requires Pd, 24·3; C, 32·8; H, 6·2%).

Bistetrammine-μ-nitro-μ-aminodicobalt(III) chloride monohydrate was prepared as described by Werner and Baselli [17] (Found: Co, 24·9; Cl, 29·7. Calc. for $H_{28}O_3N_{10}Cl_4Co_2$: Co, 24·8; Cl, 29·8%), and bistetrammine-μ-peroxy-μ-aminocobalt(III) chloride tetrahydrate as described by Werner [18] (Found: Co, 23·1; Cl, 27·3. Calc. for $H_{34}O_6N_9Cl_4Co_2$: Co, 22·9; Cl, 27·5%).

The following compounds were prepared as described by Werner: [19] trans-$[Co(en)_2(NO_2)SCN]SCN$ (Found: Co, 17·3. Calc. for $C_6H_{16}O_2N_7S_2Co$: Co, 17·3%). cis- and trans-$[Co(en)_2(NO_2)SCN]Cl$ (Found: cis-isomer, Co, 18·4; trans-isomer, Co, 18·2. Calc. for $C_5H_{16}O_2N_6ClSCo$: Co, 18·4%). cis- and trans-$[Co(en)_2(NO_2)SCN]NO_2$ (Found: cis-isomer, Co 18·1; trans-isomer, Co, 17·6. Calc. for $C_5H_{16}O_4N_7SCo$: Co, 17·9%). trans-$[Co(en)_2(NO_2)Cl]SCN$ (Found: Co, 19·0. Calc. for $C_5H_{16}O_2N_6SClCo$: Co, 18·4%).

cis-$[Co(en)_2(NO_2)Cl]NO_2$ was prepared as described by Werner and Gerb [20] (Found: Co, 19·3. Calc. for $C_4H_{16}O_4N_6ClCo$: Co, 19·2%), as was cis-$[Co(en)_2(NO_2)Cl]Cl$ (Found: Co, 19·9. Calc. for $C_4H_{16}O_2N_5Cl_2Co$: Co, 19·9%).

cis-$[Co(en)_2(NO_2)_2]NO_3$ was prepared according to Werner and Humphrey,[21] and from it the *trans*-isomer was prepared following Werner's instructions [19] (Found: cis-isomer, Co, 17·5; trans-isomer, Co, 17·5. Calc. for $C_4H_{16}O_7N_7Co$: Co, 17·7%).

cis-$[Co(en)_2(NO_2)_2]NO_2$ was prepared by a recorded method,[22] and the *trans*-isomer according

[14] Mann and Purdie, *J.*, 1936, 873.
[15] Mann and Purdie, *J.*, 1935, 1549.
[16] Mann and Wells, *J.*, 1938, 702.
[17] Werner and Baselli, *Z. anorg. Chem.*, 1898, **16**, 150.
[18] Werner, *Ber.*, 1907, **40**, 4609.
[19] Werner, *Annalen*, 1912, **386**, 1—272.
[20] Werner and Gerb, *Ber.*, 1901, **34**, 1739.
[21] Werner and Humphrey, *Ber.*, 1901, **34**, 1719.
[22] *Inorg. Synth.*, 1953, **4**, 177.

to Werner and Humphrey [21] (Found: *cis*-isomer, Co, 18·45; *trans*-isomer, Co, 18·4. Calc. for $C_4H_{16}O_6N_7Co$: Co, 18·6%).

trans-[Co(en)$_2$(NO$_2$)$_2$]I was prepared from the *trans*-nitrate by treating a solution of the latter with a warm solution of potassium iodide; the crystalline product which formed was filtered off and dried in a desiccator over sulphuric acid (Found: Co, 14·7. Calc. for $C_4H_{16}O_4N_6ICo$: Co, 14·8%).

cis- and *trans*-[Co(en)$_2$(NO$_2$)$_2$]Cl were prepared by passing the *cis*- and *trans*-nitrate complexes respectively through Amberlite I.R.A.-400 (OH⁻ form). The eluant contained the hydroxyl complex, and was neutralised with hydrochloric acid and evaporated over concentrated sulphuric acid in a vacuum-desiccator to crystallisation (Found: *cis*-isomer, Co, 19·0; *trans*-isomer, Co, 19·1. Calc. for $C_4H_{16}O_4N_6ClCo$: Co, 19·2%). *cis*- and *trans*-[Co(en)$_2$(NO$_2$)$_2$]SCN were prepared by Werner's method [19] (p. 199) (Found: *cis*-isomer, Co, 17·8; *trans*-isomer, Co, 17·8. Calc. for $C_5H_{16}O_4N_7SCo$: Co, 17·9%).

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