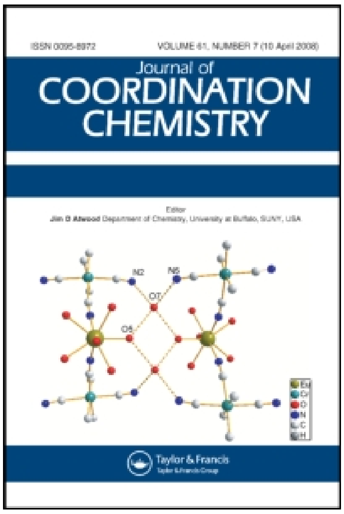


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Metal Complexes of Aniline: Infrared and Raman Spectra

David A. Thornton[a]
[a] Department of Chemistry, University of Cape Town, Rondebosch, South Africa

To cite this Article Thornton, David A.(1991) 'Metal Complexes of Aniline: Infrared and Raman Spectra', Journal of Coordination Chemistry, 24: 3, 261 — 289

To link to this Article: DOI: 10.1080/00958979109407887

URL: http://dx.doi.org/10.1080/00958979109407887

J. Coord. Chem. 1991, Vol. 24. pp. 261-289
Reprints available directly from the publisher
Photocopying permitted by license only

METAL COMPLEXES OF ANILINE: INFRARED AND RAMAN SPECTRA

DAVID A THORNTON

Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa.

(Received 30 May, 1989)

The literature for the years 1965–1987 has been searched for all significant papers which refer to the vibrational spectra of metal complexes of aniline and substituted anilines. These papers have been reviewed with particular reference to isotopic labelling and metal ion substitution studies as assignment techniques and to the structural and bonding information which can be derived from the spectra. Compounds of the following classes are included: $[M(an)_2X_2]$ (M = Mn, Co, Ni, Cu, Zn, Cd, Hg; an = aniline, X = Cl, Br, I, NCS); *cis*- and *trans*-$[Pt(an)_2X_2]$ (X = Cl, Br, I, NO_2); $[M(R\text{-}an)_2X_2]$ (M = Mn, Co, Ni, Cu, Zn; R-an = *o*-, *m*- and *p*-toluidine and other substituted anilines; X = Cl, Br, I); aniline adducts of metal β-ketoenolates; the complexes *trans*-$[PtL(R\text{-}an)X_2]$ (L = $CH_2{=}CH_2$ or CO, R-an = aniline or a substtuted aniline, X = Cl, Br); and other miscellaneous systems comprising aniline as a ligand.

Keywords: Aniline complexes, vibrational spectra, isotopic labelling, transition metals, infrared, Raman

1. INTRODUCTION AND SCOPE OF THE REVIEW

By contrast with the extensive literature on the vibrational spectra of metal complexes of pyridine (py), those of aniline (an) have been studied to a lesser extent despite the importance of aniline and substituted anilines to the field of coordination chemistry. Thus, the most recent edition of Nakamoto's text (1986)[1] does not mention the spectra of these complexes and the earlier standard texts dating from 1967 (Adams)[2] and 1971 (Ferraro)[3] include brief descriptions of the earliest infrared papers only.

The first comprehensive reports on the vibrational spectra of aniline complexes were published in 1965.[4,5] They gained an advantage over pyridine complexes by virtue of the fact that metal–aniline stretching frequencies are some 100 cm^{-1} higher than metal-pyridine stretches. Thus, progress on the vibrational spectra of aniline complexes did not have to await the advent of commercial far-infrared interferometers which so delayed corresponding studies of pyridine complexes.

In this review, the author hopes to have included reference to all existing papers (up to the end of 1987) on the vibrational spectra of aniline complexes in which the question of band assignments or structural and bonding aspects of the spectra comprises a major feature of the work reported. Particular attention is given to isotopic labelling and the effects of metal ion substitution as assignment techniques. Papers in which the spectra of one or two aniline complexes are mentioned incidentally or which are confined to the internal ligand modes only, have generally been excluded. The indispensable series: *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Volumes 1–20, published by the Royal Society of Chemistry, has been employed as a source of references to the field. These volumes cover the literature for the years 1967–1986.

2. THE SPECTRA OF ANILINE AND THE COMPLEXES $[Zn(an)_2X_2]$ (X = Cl, Br, I): DEUTERATION AND ^{15}N-LABELLING

The tetrahedral zinc(II) complex $[Zn(an)_2Cl_2]$ is chosen for initial discussion because it has been the subject of a complete ir analysis over the range 4000–50 cm^{-1} including a study[6] of the effects of ^{15}N-, d_2-, d_5- and d_7-labelling (Figs. 1 and 2). Furthermore, the spectrum of this complex has been discussed in relation to the most complete study published on the ir and Raman spectra of aniline and aniline-d_2 by Evans in 1960.[7]

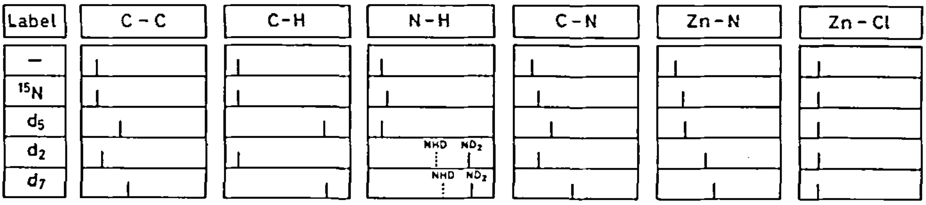


FIGURE 1 Qualitative depiction of expected effects of the various types of labelling on vibrations involving the C–C, C–H, N–H, C–N, Zn–N and Zn–Cl bonds in $[Zn(an)_2Cl_2]$.

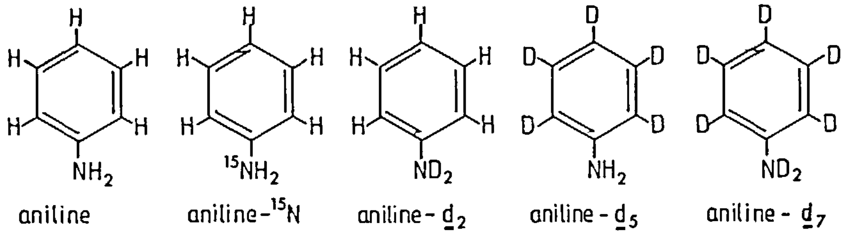


FIGURE 2 Labelled forms of aniline.

In matching the spectrum of $[Zn(an)_2Cl_2]$ with the spectrum of liquid aniline reported by Evans (Table I), it is observed that 17 of the 23 ligand bands move to lower frequency on coordination. The six bands which move to higher frequency comprise ring modes and the NH_2 twisting and wagging modes. The NH_2 scissoring mode and, as expected, the N–H stretching modes, move to lower frequency on coordination, the latter by 175 cm^{-1} (antisymmetric νN–H) and 139 cm^{-1} (symmetric νN–H).

Only two crossovers occur between the frequencies of the aniline bands and those of the complex. These arise between the first aromatic ring band and the NH_2 scissoring mode near 1600 cm^{-1} and again between the δC–H bands in the 1000–1100 cm^{-1} region and the NH_2 twist at 1104 cm^{-1} (Table I). Apart from these situations, the order of frequencies of the complex matches that of the ligand.

Deuteration of the ligand (whether d_2- d_5- or d_7-) causes substantial shifts in the NH_2 modes but smaller shifts (if any) in the ring and C–H modes (Fig. 1). Because of

TABLE I
Frequency data (cm^{-1}) and assignments for aniline, $[Zn(an)_2Cl_2]$ and its labelled analogues

Aniline[a]	$[Zn(an)_2Cl_2]$							Assignment
A	Un-labelled B	^{15}N C	d_5 D	d_2 E	d_7 F	Ratio D/B	Ratio E/B	
3440	3265	3256	3263	2442(NHD)	2444(NHD)	1.00	0.75	ν(N-H)
				2391(ND_2)	2394(ND_2)		0.73	
3360	3221	3215	3219	2409(NHD)	2409(NHD)	1.00	0.75	
				2348(ND_2)	2353(ND_2)		0.73	
3212	3128	3122	3126	2277	2314	1.00	0.73	ν(N-H---N(Cl))
3071	3039	3039	2277	3033	2280	0.75	1.00	ν(C-H)
3037	3018	3017	2266	3010	2265	0.75	1.00	
1618	1578	1574	1570	1246(NHD)	1206(NHD)	0.99	0.79	NH_2 scissor
				1107(ND_2)	1108(ND_2)		0.70	
1600	1605	1604	1586	1603	1569	0.99	0.99	ν(ring)
1500	1493	1492	1385	1493	1387	0.93	1.00	
1468	1470	1469	1370	1460	1349	0.93	0.99	
1278	1218	1215	1159	1216	1116	0.95	1.00	ν(C-N)
1175	1146	1146	843	1141	843	0.73	1.00	δ(C-H)
1154	1071	1071	820	1075[b]	821	0.76	1.00	
1071	1025	1025	763	1024	753	0.74	1.00	
1028	1003	1003	747	1002	(753)	0.74	1.00	
1050	1104	1101	1107	917(NHD)	889(NHD)	1.00	0.83	NH_2 twist
				866(ND_2)	860(ND_2)		0.78	
970	902	902	648	890	630	0.72	0.99	γ(C-H)
880	799	794	595	788	596	0.74	0.99	
826	757	755	559	742	556	0.74	0.98	
751	695	693	471	693	454[b]	0.68	1.00	
670	673	667	673	536(NHD)	532(NHD)	1.00	0.79	NH_2 wag
				511(ND_2)	522(ND_2)		0.76	
	661	655	660	528(NHD)	(522)(NHD)	1.00	0.80	
				503(ND_2)	513(ND_2)		0.76	
618	619	619	595	619	576	0.96	1.00	δ(ring)
501	534	533	528	(536)	(513)	0.98	0.99	
	527	523	525	404(NHD)	387(NHD)	0.99	0.76	NH_2 rock
				387(ND_2)	378(ND_2)		0.73	
	406	398	388	336	330	0.96	0.84	ν(Zn-N)
	366	361	352	322	316	0.96	0.89	
	298	297	298	295	295	1.00	0.99	ν(Zn-Cl)
	273	273	273	273	273	1.00	1.00	
230	225	225	213	225	213	0.95	1.00	γ(ring)
	205	205	193	205	194	0.94	1.00	
	132	132	132	132	132	1.00	1.00	δ(Cl-Zn-Cl)
	115	114	111	111	108	0.97	0.97	δ(N-Zn-N)
	102	102	101	101	100	0.99	0.99	δ(N-Zn-Cl)
	89	88	86	88	85	0.97	0.99	

[a] Frequencies from paper by Evans,[7] except band at 230 cm^{-1} [6]

[b] Mean of doublet.

this, there are numerous crossovers of the ND_2 bands in the d_2- and d_7-labelled complexes as Fig. 3 shows. Further complications arise from partial hydrogen–deuterium exchange ($NH_2 \rightarrow NHD + ND_2$) which leads to doubling of the amino group bands in the d_2- and d_7-labelled complexes. The simplest way of distinguishing between the NH_2 and ring modes is by ^{15}N-labelling since the shifts on introducing the ^{15}N isotope are much smaller than those which occur on deuteration. The author strongly recommends this technique to those who would study the vibrational spectra of aniline complexes, especially in view of the commercial availability of aniline-^{15}N at a reasonable price. The ^{15}N-labelled shifts lie between 0 and 9 cm^{-1}. As expected from the diatomic molecule relationship: $\nu = k(f/\mu)^{\frac{1}{2}}$ (k = constant, f = force constant, = reduced mass) the υN–H bands shift most (between 6 and 9 cm^{-1}) while the NH_2 bending modes (scissor, twist, wag and rock) shift between 3 and 6 cm^{-1}. There are only three anomalously shifted bands (the γC–H modes between 690 and 800 cm^{-1}), a phenomenon which probably arises from vibrational coupling.

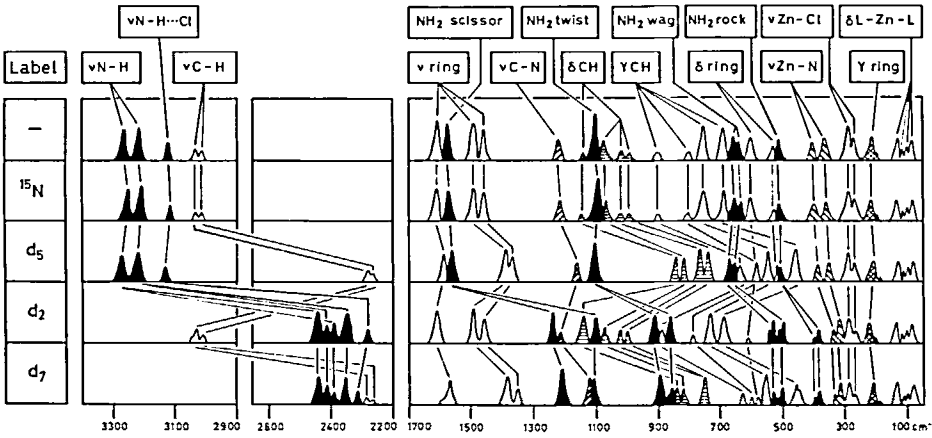


FIGURE 3 The i.r. spectra of $[Zn(an)_2Cl_2]$ and its labelled analogues.

Deuteration of the aniline ring (d_5) or amino group (d_2) enables a ready distinction to be made between the C–H and ring modes of the aromatic ring. In 1979, Thornton and colleagues[8] examined the ratio ν^D/ν^H between the frequencies of corresponding bands in the spectra of normal and deuterated molecules of several nitrogenous ligands and their complexes. It was found that ν^D/ν^H falls within the ranges 0.68 to 0.85 for C–H vibrations and 0.85 to 1.00 for ring modes. Thus, determination of the ratio affords a ready method for distinguishing between these two classes of vibrational modes. Table I includes the values for the ν^D/ν^H ratio for the d_2- and d_5-labelled complexes. It is observed that, on the basis of the assignments proposed, the values of the ratio fall within the ranges cited above. Furthermore, the ratio for the NH_2 modes is close to unity for d_5-labelling as would be expected for deuteration at a site remote from the NH_2 group but much lower for d_2-labelling where deuteration occurs at the amino group.

The far-ir spectra of aniline complexes are simplified by the fact that aniline has ony one vibrational mode with a frequency less than 450 cm^{-1}. This is the γ-ring band at 230 cm^{-1} which is doubled in the spectrum of the complex $[Zn(an)_2Cl_2]$, the two peaks occurring at 225 and 205 cm^{-1}. Apart from these two bands, eight peaks are observed within the range 450–50 cm^{-1}. For the C_{2v} symmetry of this tetrahedral molecule, eight bands are anticipated: two νZn–N, two νZn–Cl and four δL–Zn–L bands.

Table II lists the band shifts which occur for the four modes of labelling and also those which occur on substitution of Cl by Br or I. On the basis of these shifts, there is no ambiguity in establishing the correct assignments. Even the bending modes may be distinguished in this way.

TABLE II
Shifts (cm^{-1}) induced by isotopic labelling and halogen substitution in low-frequency bands of [Zn(an)$_2$Cl$_2$]

Frequency unlabelled	Shift[a]						Assignment
	^{15}N	d_5	d_2	d_7	Br	I	
406	8	18	70	76	3	8	ν(Zn–N)asym (b_1)
366	5	14	44	50	9	22	ν(Zn–N)sym (a_1)
298	1	0	3	3	86	112	ν(Zn–Cl)asym (b_2)
273	0	0	0	0	81	118	ν(Zn–Cl)sym (a_1)
225	0	12	0	12	0	2	γ(ring)
205	0	12	0	11	–[b]	3	
132	0	0	0	0	9	19	δ(Cl–Zn–Cl) (a_1)
115	1	4	4	7	0	3	δ(N–Zn–N) (a_1)
102	0	1	1	2	9	21	δ(N–Zn–Cl) (b_1, b_2)
89	1	3	1	4	15	22	

[a] All shifts are to lower wavenumber.
[b] Masked by ν(Zn–Br)asym band.

A comparison between the frequency data for the complexes [Zn(an)$_2$X$_2$] and [Zn(py)$_2$X$_2$] is of interest (Table III). The νZn–N frequencies are much higher for the aniline complex. This is, at least partly, a result of the mass effect if we consider that the zinc(II) ion is effectively "vibrating against" the NH$_2$ group (mass: 16 amu) in the aniline complex and against the pyridine molecule (mass: 79 amu) in the pyridine complex. By contrast, the νZn–X values are more comparable for the pyridine and aniline complexes where the mass effects are similar.

TABLE III
Comparison of the metal-ligand frequency data for the complexes [ZnL$_2$X$_2$] (L = aniline, pyridine; X = Cl, Br, I) (cm^{-1})

Band	[Zn(an)$_2$X$_2$]			[Zn(py)$_2$X$_2$]		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
νZn-N asym (b_1)	406	403	398	217	218	213
νZn-N sym (a_1)	366	357	344	200	182	165
νZn-X asym (b_2)	298	212	186	331	260	222
νZn-X sym (a_1)	273	192	155	296	213	147
δN-Zn-N (a_1)	115	115	113	154	151	154
δX-Zn-X (a_1)	132	123	(113)	Beyond limit of measurement		
δN-Zn-X (b_1,b_2)	102	93	82			
	89	74	67			

3. THE COMPLEXES [M(an)$_2$X$_2$] (M = Mn, Co, Ni, Cu, Zn, Cd; X = Cl, Br, I).

The earliest ir studies on the complexes of formula [M(an)$_2$X$_2$] were made in 1965.[4,5] Jungbauer and Curran[4] determined the spectra of 19 complexes of the metal(II) ions Mn, Co, Ni, Cu, Zn, Cd, Pd and Pt. However, most of the discussion related to the amino group vibrations, the low frequency limit being 250 cm^{-1}. Some d_2-labelled complexes were included and these assisted the assignment of the internal ligand modes. Concerning the metal–ligand modes, νM–X was assigned for six of the complexes studied and the reslts are generally in good agreement with those subsequently obtained by other workers using more sophisticated techniques (Table IV). No specific assignments for the νM–N modes were reported but bands within the range 450–370 cm^{-1} were found to shift by an average of 12 cm^{-1} on ND$_2$-deuteration and their frequencies were observed to be metal-sensitive in the sequence Pt > Pd > Cu > Co > Mn > Zn > Cd which suggested that they were associated with νM–N.

TABLE IV
Comparison of the νM–N and νM–X frequency data from eight studies of the ir spectra of [M(an)$_2$X$_2$] complexes

Complex	Mode	Thornton[9]	Ahuja[5]	Goldstein[10,11]	Others[4,12–14]
Mn(an)$_2$Cl$_2$	νM–N		386	386[a]	370[e]
			374	318[a]	
	νM–Cl		227	239[a]	318[c]
				216	
Mn(an)$_2$Br$_2$	νM–N		367	380[a]	371[e]
			350	329[a]	
	νM–Br		n.o.	162	
				152	
Mn(an)$_2$I$_2$	νM–N		361		
			355		
Co(an)$_2$Cl$_2$	νM–N	416	415	413	413,[d] 414[e]
		367	366	365	365,[d] 364[e]
	νM–Cl	319	318		319,[c], 319[e]
		303	299		297,[c] 299[e]
Co(an)$_2$Br$_2$	νM–N	416	412		
		395	358		
	νM–Br	242	245		
		221			
Co(an)$_2$I$_2$	νM–N		410		
			349		
	νM–I		~208		
Ni(an)$_2$Cl$_2$	νM–N	379	383[a]	391[a]	390,[d] 375[e]
		349	350	348[a]	
	νM–Cl	235	238	253	
		208		237	207[c]
Ni(an)$_2$Br$_2$	νM–N	381[a]	378[a]	387[a]	
		350	354	354[a]	
	νM–Br	199	n.o.	188	
		176		179	
Ni(an)$_2$I$_2$	νM–N		361		
			345		

TABLE IV (*continued*)

omplex	Mode	Thornton[9]	Ahuja[5]	Goldstein[10,11]	Others[4,12–14]
$u(an)_2Cl_2$	νM-N	434	430	n.r.	430[d]
		359	357	361	
	νM-Cl	310	306	313	306[c]
		235			
$u(an)_2Br_2$	νM-N	431	424	–	
		352	348	354	
	νM-Br	230	233	242	
		–	–	–	
$n(an)_2Cl_2$	νM-N	406	402		400,[d] 406[e]
		366	362		363,[d] 366[e]
	νM-Cl	298	294		295,[c] 297[e]
		273			287[c]
$n(an)_2Br_2$	νM-N	403	400		401[e]
		357	355		357[e]
	νM-Br	212	230		234[e]
		192			209[e]
$n(an)_2I_2$	νM-N	398	396		397[e]
		344	342		344[e]
	νM-I	186	n.o.		
		155			
$d(an)_2Cl_2$	νM-N		377	382[a]	373[e]
			351	320[a]	
	νM-Cl		n.r.	216[a]	
				187[a]	
$d(an)_2Br_2$	νM-N		365	373	368[e]
			350	324	
	νM-Br		n.r.	187[a]	
				140	
$d(an)_2I$	νM-N		370	210[b]	377[e]
			339	197[b]	341[e]
	νM-I		n.r.	155[b]	
				140[b]	
$g(an)_2Cl_2$	νM-N				370,[f] 372[e]
	νM-Cl				297[f]
$g(an)_2Br_2$	νM-N				365[f]
					345[f]

Mean of split band
At ca. 100K[11]
Jungbauer and Curran[4]
Noji and Kidani[12]
Akyüz and Davies[13]
Ahuja and Rastogi[14]

Also in 1965, Ahuja *et al.*[5] determined the uv and ir spectra of a wide range of omplexes $[M(an)_2X_2]$ (M = Mn, Co, Ni, Cu, Zn, Cd; X = Cl, Br, I). The uv eflectance spectra were used to assign structures to these compounds. On their basis, he Mn(II) and Ni(II) complexes were assigned polymeric octahedral structure with ridging halides, the Cu(II) complexes being similar but tetragonally-distorted by the ahn–Teller effect. The Co(II)complexes are tetrahedral like those of Zn(II). The ir spectra were confined to the far-ir region 600–200 cm^{-1}. The assignments were made on a purely empirical basis. Two (occasionally three) bands were assigned to νM–N within the range 430–330 cm^{-1}. The νM–X bands could only be assigned for one-third of the complexes studied. Four monomeric bis(ethanol) adducts of formula [M(an)$_2$(ethanol)$_2$X$_2$] (M = Mn, Ni; X = Cl, Br) were included. For these, νM–O was reported in the 480–460 cm^{-1} region. Except for the complexes of Mn(II) and Cd(II), the agreement of the results of Ahuja *et al.* with those of other workers is generally good (Table IV).

In 1978, the ^{15}*N*-labelling study which had successfully been applied to the ir spectra of [Zn(an)$_2$X$_2$][6] (Section 2) was extended to the corresponding complexes of Co(II), Ni(II) and Cu(II) by Thornton *et al.*[9] ^{15}*N*-Labelling, halide substitution and the effects of metal-ion substitution were used for the assignments of the internal ligand modes and the metal-ligand vibrations. The spectra are depicted in Fig. 4 and the frequency and shift data are reported in Table V. The lower limit of this work was 140 cm^{-1}. The amino group modes were assigned on the basis of the ^{15}*N*-shifts; they were observed in regions similar to those reported for [Zn(an)$_2$Cl$_2$]. The νM–N modes were assigned to two bands within the range 440–340 cm^{-1} which exhibited shifts of between 2 and 8 cm^{-1} towards lower frequency on ^{15}*N*-labelling and which were relatively insensitive towards X-substitution. The two νM–Cl bands were within the range 320–200 cm^{-1}. They were unaffected by ^{15}*N*-labelling but shifted to the range 240–175 cm^{-1} on substitution of Br for Cl.

TABLE V

Frequencies and ^{15}N-induced shifts (in parentheses) of aniline and the complexes [M(an)$_2$X$_2$](cm^{-1})[a]

Aniline[b]	M = Co	M = Ni	M = Cu	M = Zn	M = Zn	Assignment
[M(an)$_2$Cl$_2$]						
3440	3262(11)	3311(7)[c]	3307(9)	3265(9)		ν(N–H)asym.
3376	3216(10))	3249(8)[d]	3231(5)	3221(6)		ν(N–H)sym.
3212	3126(8)	3132(5)	3161(2)	3128(6)		ν(N–H---N(Cl))
1618	1577(5)	1572[e]	1567(4)	1578(4)		NH$_2$ scissor
1600	1604	1602	1602	1605		ν(ring)[f]
1278	1220(4)	1240(8)[g]	1221(5)	1218(3)		ν(C–N)
1175	1144(2)	1150[e]	1143(2)	1146		δ(C–H)
1154	1072	1064	1066	1071		
1071	1025		1029	1025		
1028	1003	999	1003	1003		
1050	1103(8)	1043(4)	1089(7)	1104(3)		NH$_2$ twist
970	902	891	901	902		δ(C–H)
880	799(7)[h]	804(6)[gh]	804(7)[h]	799(5)[h]		
826	755	749	752	757(2)		
751	693	692[g]	692	695(2)		
694	665(6)	628(3)	682(6)	673(6)		NH$_2$ wag
670	652(7)			661(6)		
618	619	613	620(2)	619		δ (ring)
501	533(3)	522		534		
	525(4)	544(6)	535(4)	527(4)		NH$_2$ rock
	416(6)	379(4)	434(6)	406(8)		ν(M–N)
	367(4)	349(4)	359(2)	366(5)		
	319	235	310(2)	298		ν(M–Cl)
	303	208	235(2)	273		

TABLE V

Aniline[b]	M = Co	M = Ni	M = Cu	M = Zn	M = Zn	Assignment
230	227	(235)	(235)	225		γ (ring)
		185		205		
	150	168	168(2)			δ(L–M–L)
$[M(an)_2Br_2]$					$[Zn(an)_2I_2]$	
3440	3257(12)	3308(8)	3294(11)	3260(7)	3268(8)	ν(N–H) asym.
3376	3210(7)	3236(7)[j]	3232(9)	3219(7)	3215(6)	ν(N–H) sym.
3212	3115(7)	3136(12)	3157(3)	3118(7)	3105(8)	ν(N–H---N(X))
1618	1570(5)	1568(5)	1562(5)	1571(5)	1564(4)	NH_2 scissor
1600	1603	1603	1601	1603	1602	ν(ring)[f]
1278	1218(5)	1227(4)[g]	1219(6)	1217(4)	1214(4)	ν(C–N)
1175	1139(4)	1150[e]	1142(5)	1141(3)	1132(3)	δ(C–H)
1154	1070	1066	1067	1071	1068	
1071	1026		1029	1024	1028	
1028	1001	999	1004(2)	1002	1002	
1050	1099(5)	1046(4)	1090(8)	1102(5)	1090(7)	NH_2 twist
970	902	891	902	901	900	δ(C–H)
880	798(7)[h]	804(6)[h]	803(8)[h]	798(4)[h]	798(6)[h]	
826	754	750	752	753	754	
751	693	693[g]	692	692	693	
694	658(7)	627(4)	676(6)	663(5)	647(5)	NH_2 wag
670	644(6)	609(4)		651(7)	636(5)	
618	618		619	618	616	δ(ring)
	532(3)	544(7)	535(4)	540(7)	538(6)	NH_2 rock
	524(4)	525(4)		525(3)	520(2)	
	416(8)	372(4)[k]	431(6)	403(6)	398(6)	ν(M–N)
	395(3)	350(7)	352(4)	357(2)	344(3)	
	242	199	230	212	186	ν(M–X)
	221	176		192	155	
230	(221)	210sh	(230)	225	223	γ(ring)
	191		158		155	

[a] Absence of shift data implies a shift ≤1 cm^{-1}. Data for $[Zn(an)_2Cl_2]$ from [6]. [b] Frequencies for aniline from [7]. [c] Shoulder at 3320(8) cm^{-1}. [d] Shoulder at 3240(5) cm^{-1}. [e] Too broad for determination of ^{15}N-shift. [f] Two additional ν(ring) bands near 1490 and 1470 cm^{-1} [6] are masked by nujol bands. [g] Mean of doublet. [h] Assigned to γ(C–H) despite observed ^{15}N-shift since corresponding band shifts only 11 cm^{-1} in spectrum of $[Zn(an\text{-}d_2)_2Cl_2]$ compared with 238 cm^{-1} shift in NH_2 twist. [i] Shoulder at 392(3) cm^{-1}. [j] Shoulder at 324(6) cm^{-1}. [k] Shoulder at 389(4) cm^{-1}.

The νM–N and νM–X bands vary in the sequences Co > Ni < Cu > Zn for one band and Co > Ni < Cu < Zn for the other. The increased coordination number (CN) which accompanies substitution of Co (CN = 4) by Ni (CN = 6) is expected[15] to lead to a decrease in νM–L as is observed for both νM–N and both νM–X bands. Despite the fact that the Ni(II) and Cu(II) complexes have the same CN, replacement of Ni by Cu is expected[16] to cause an increase in νM–L because of the additional stablilization accompanying the tetragonal Jahn–Teller distortion of the Cu complex (or the reduced CN if it is *trans*-square planar as has been proposed by others[10]). This is also observed for all the νM–N and νM–X bands. Replacement of Cu(II) by Zn(II) leads to a reduction in CN (assuming tetragonal structure for the copper complex) which would tend to increase νZn–L and a decrease in crystal field stabilization energy (CFSE) which would tend to reduce νZn–L.[17] These opposing influences cause some νM–L bands to increase and others to decrease with the shift either way, being smaller than those resulting from the metal ion substitutions discussed above.

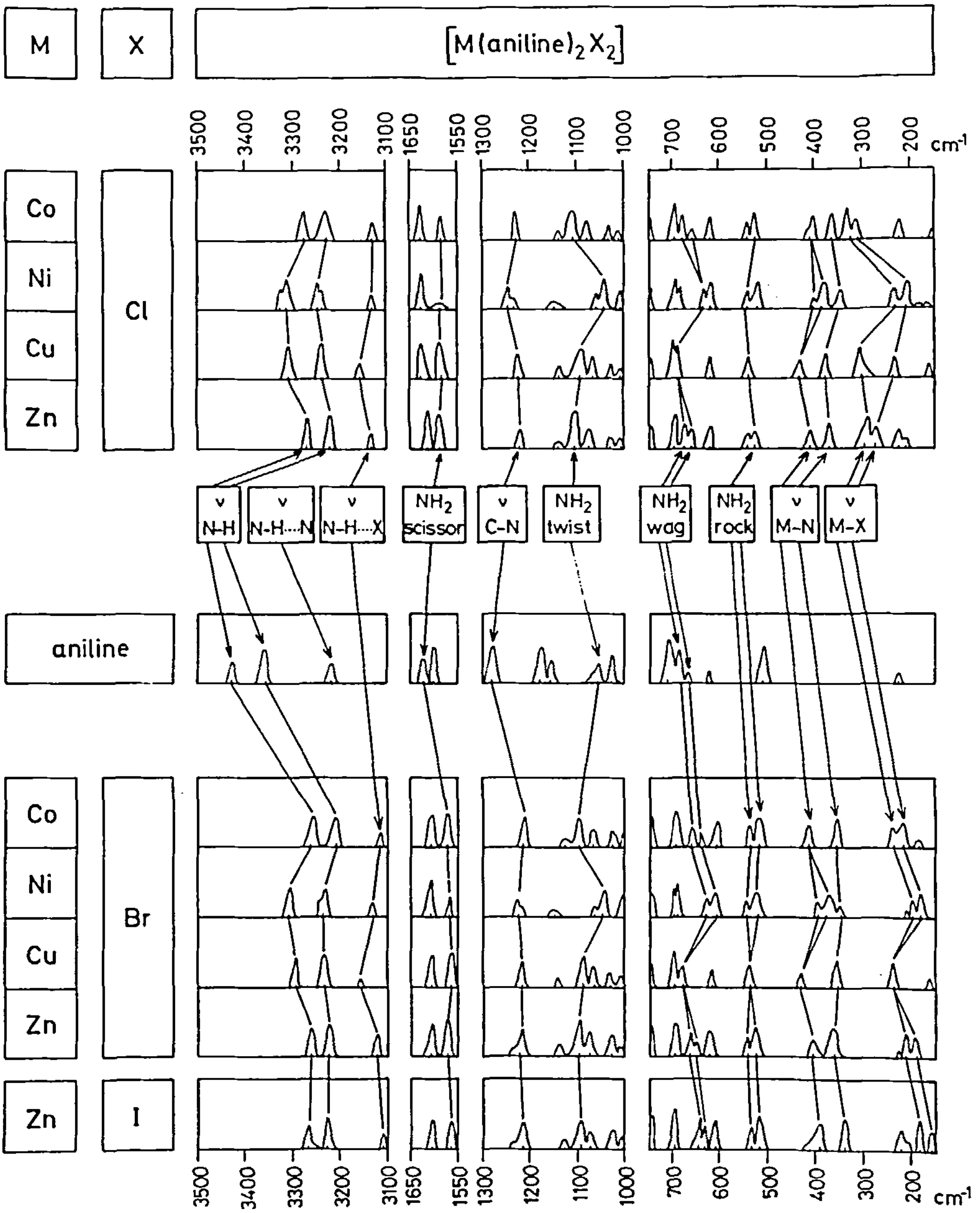


FIGURE 4 Infrared spectra of aniline complexes [M(an)$_2$X$_2$]. Spectrum of Zn(an)$_2$Cl$_2$] from ref. 6.

As a corollary to these metal ion substitution effects, the ir spectra of the complexes $[M(an)_2(ethanol)_2Cl_2]$ (M = Co, Ni) have been studied (Fig. 5).[9] The transformation $[Co(an)_2Cl_2] \rightarrow [Co(an)_2(ethanol)_2Cl_2]$ leads to an increase in CN and a decrease in CFSE. Both effects will tend to reduce the νM–L frequencies. This is observed (νCo–N shifts from 416, 367 cm^{-1} to 391, 353 cm^{-1} and νCo–Cl moves from 319, 303 cm^{-1} to 212, 203 cm^{-1}). The marked reduction in νCo–Cl indicates relatively weak Co–Cl bonding in the ethanol adduct. By contrast, the occurrence of νCo–O at 474 cm^{-1} indicates that the bonding between Co and ethanol is quite strong.

The transformation of $[Ni(an)_2Cl_2]$ into its *bis*(ethanol) adduct leads to no change in CN (both complexes are octahedral) and both complexes have similar CFSEs. As a result, the observed shifts in νNi–N and νNi–Cl are much smaller than those which occur in the cobalt complexes.

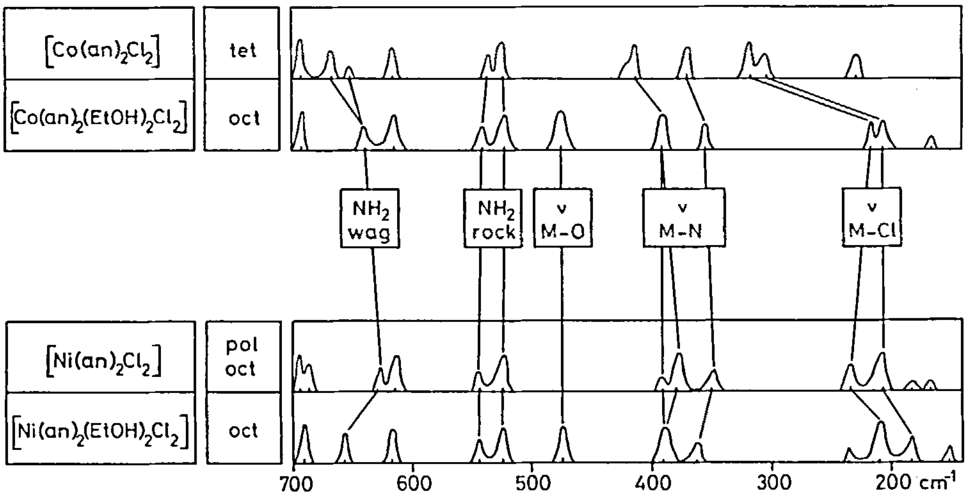


FIGURE 5 Comparison of infrared spectra of $[M(an)_2Cl_2]$, and $[M(an)_2(ethanol)_2Cl_2]$, tet = tetrahedral, oct = octahedral, pol oct = polymeric octahedral.

In 1980, Goldstein and Hughes,[10] (without reference to the 1978 paper of Thornton *et al.*[9]) discussed the far-ir spectra (400–30 cm^{-1}) of several aniline complexes $[M(an)_2X_2]$ (M = Mn, Ni, Cu, Cd; X = Cl, Br) and their deuterated (d_2) analogues. The Raman spectra of the Cd(II) complexes were also reported. The effects of deuteration, expressed as the ν^{H}/ν^{D} ratio, were used to distinguish between the νM–N and νM–X bands and to make some skeletal deformation assignments. The metal-ligand assignments (Table IV) confirmed octahedral polymeric structure for the Mn(II), Ni(II) and Cd(II) complexes but the Cu(II) complexes were considered to be *trans*-square planar rather than polymeric tetragonal, only one νM–N and one νM–X band being assignable in their spectra. A crystallographic study of this complex would be of interest.

In 1982, Akyüz and Davies[13] reported the ir (4000–200 cm^{-1}) and Raman (3500–50 cm^{-1}) spectra of a range of complexes $[M(an)_2X_2]$ (M = Mn, Co, Ni, Zn, Cd, Hg; X variously = Cl, Br, I). Assignments were proposed for all of the observed bands. Again, the elusive paper by Thornton *et al.* in 1978[9] was not referred to. No labelling studies were made but the interesting assignment technique originally proposed by Lever and Ramaswamy[18] for certain metal-pyridine complexes was extended to these aniline complexes. This consists of observing the shift in the ir band which occurs on cooling the mulled sample to *ca.* 83 K. It was noted that, whilst the aniline ring and C–H modes are virtually insensitive to temperature, the NH_2 rocking mode and the νM–L modes increase with decreasing temperature. By contrast, the frequencies of the N–H stretching modes decrease at low temperature. Positive shifts of between 4 and $10\,cm^{-1}$ are observed for the νM–N and νM–X bands. Unfortunately, the neighbouring NH_2 rocking modes also shift by a similar magnitude and are therefore not distinguished from the νM–N bands by this technique. An extension of this method to the ir spectra of other coordination compounds would be of interest. the frequency data resulting from the work of Akyüz and Davies is compared with the earlier reported assignments in Table IV.

4. THE COMPLEXES $[M(an)_2(NCS)_2]$ (M = Co, Ni, Cu, Zn)

The assignment problem in this series of compounds exceeds those of the halide complexes discussed in Section 3 in respect of the additional internal ligand bands conferred by the presence of the isothiocyanate ligands and by the existence of two species of νM–N bands which are distinguished in this discussion by νM–N and νM–NCS. Engelter and Thornton[19] labelled both nitrogen atoms with the ^{15}N-isotope in order to distinguish between the coordination of the two ligands. The spectra and the resulting assignments are depicted in Fig. 6 with the spectra of aniline and NaSCN shown for comparison. The frequencies of principal interest and the relevant shift data are given in Table VI.

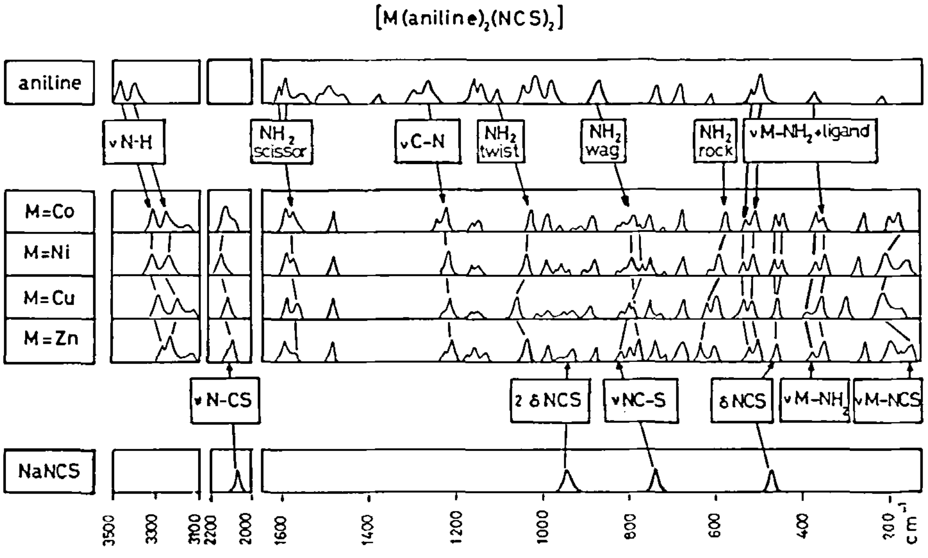


FIGURE 6 Infrared spectra of the complexes $[M(an)_2(NCS)_2]$.

TABLE VI

Infrared frequencies (cm^{-1}) of complexes [$ML_2(NCS)_2$] (L = aniline)[a]

	Ligand					
Vibration	NaSCN	Aniline[b]	M = Co	M = Ni	M = Cu	M = Zn
νN-H asym		3481(10)	3324(0,9)	3325(0,9)	3300(0,9)	3279(0,6)
νN-H sym		3395(5)	3252(2,8)	3254(0,6)	3218(3,8)	3235(0,6)
νN-H---N			3153(0,8)		3128(0,8)	3138(0,6)
νN-CS[c]	2074(26)		2123(29,2)	2131(27,0)	2118(28,2)	2100(29,0)
NH_2 scissor		1619(6)	1589(0,5)	1590(0,4)	1578(0,4)	1591(0,3)
νC-N		1276(5)	1234(0,4)	1238(3,8)	1232(0,5)	1223(0,4)
NH_2 twist		1115(2)	1043(0,2)	1051(0,4)	1077(0,6)	1050(0,4)
2δ NCS	960(7)		922(7,0)			948(7,0)
NH_2 wag		884(2)	805(0,7)	806(0,6)	808(6,6)	798(0,6)
νNC-S	756(10)		784(11,0)	779([d],0)	815(5,0)	833(11,0)
NH_2 rock			588(0,5)	602(0,5)	638(0,7)	648(0,6)
νM-NH_2 + ligand			541(0,6)	544(0,5)	550(0,6)	534(0,6)
		529(6)	520(0,2)	523(0,2)	532(0,4)	520(0,3)
		382(0)	361(0,8)	361(0,4)	370(0,3)	367(0,3)
νM-NH_2			376(0,4)	380(0,4)	403(0,6)	390(0,6)
δNCS	481(4)		471(4,0)	471(4,0)	465(3,0)	470(4,0)
			461(3,0)	460(4,0)		
νM-NCS			186(4,0)	227(2,0)	231(2,0)	167(4,0)

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses in the order (^{15}NCS shift, $^{15}NH_2$ shift). Shifts < 1 cm^{-1} are not considered significant and are cited as zero shifts. All shifts are reported to the nearest integral values and are to lower frequencies.

[b] Frequencies > 1000 cm^{-1} from spectra of 0.05 M CCl_4 solutions. Frequencies < 1000 cm^{-1} from liquid film

[c] Sharp shoulders on these bands are omitted.

[d] Band disappears on ^{15}NCS-labelling.

These complexes have the same structures as the corresponding halides except for the pink Co(II) complex which is now polymeric octahedral rather than tetrahedral. The Ni(II) complex is polymeric octahedral. The Zn(II) complex is tetrahedral and the Cu(II) complex is polymeric tetragonal. However, not all of the bands expected on theoretical grounds were observed within the range studied (to 150 cm^{-1}). The distinction between νM-N and νM-NCS was readily made on the basis of the two modes of isotopic labelling and there is apparently little vibrational coupling between the two species of metal ligand stretching modes; less, in fact, than occurs in the corresponding pyridine complexes.[20] This is undoubtedly because of the large separation between the νM-N and νM-NCS modes in the aniline complexes whereas the frequencies are much more similar in the pyridine complexes. In the isothiocyanate-aniline complexes, there is, however, evidence of considerable coupling between νM-N and internal aniline ligand modes in three of the bands.

So far as metal ion substitution is concerned, it is interesting to note the difference in the effect of substitution of Co(II) by Ni(II) between the halide and isothiocyanate complexes. The relevant data are highlighted in Table VII. The transformation of the cobalt halide into the nickel halide complex leads to a decrease in the νM-L bands principally because of the increase in CN. The transformation of the cobalt isothiocyanate into the nickel isothiocyanate complex, on the other hand, involves no change in CN but an increase in CFSE which results, not only from the metal ion substitution, but also from the replacement of Cl^- by NCS^-, the latter ligand having a higher ligand field strength.[21] The result is an increase in νM–L. A corresponding study of the complexes $[M(p\text{-toluidine})_2(NCS)_2]$ has been made with similar results.[19]

TABLE VII
Comparison of effects of substitution of Co(II) by Ni(II) in chloride and isothiocyanate aniline complexes

	$[Co(an)_2Cl_2]$	→	$[Ni(an)_2Cl_2]^9$	$[Co(an)_2(NCS)_2]$	→	$[Ni(an)_2(NCS)_2]^{19}$
Band	tetrahedral	→	octahedral	octahedral	→	octahedral
νM-N	416		379	361[a]		361[a]
	367		349	376		380
νM-X	319		235	186		227
	303		208	[b]		[b]

[a] Coupled with aniline ligand mode
[b] Not observed

5. THE COMPLEXES *cis*- AND *trans*-$[Pt(an)_2X_2]$ (X = Cl, Br, I, NO_2)

Only one infrared study[22] has been made of these complexes but it is a complete one covering the range 4000–90 cm^{-1} and involving both ^{15}N-labelling and d_5-deuteration of aniline. The ^{15}N-labelling served best for the assignment of the amino group vibrations which shift much less on introducing this isotope than they do on d_5-labelling of the aromatic ring. The latter technique serves best for distinguishing between the aniline ring modes and the aromatic C–H modes, using the ν^D/ν^H ratio (see Section 2). The far-ir spectra are depicted in Fig. 7 and the frequencies are given in Table VIII.

The shifts in the N–H bands on ^{15}N-labelling are between 3 and 11 cm^{-1} in the halide complexes and there is very little difference between the *cis*- and *trans*-complexes in the mid-ir region. The ν^D/ν^H ratio spans the values 0.68 to 0.83 for C–H modes and 0.83 to 1.03 for ring modes. The internal NO_2^- modes are uniquely observed in the spectra of *cis*- and *trans*- $[Pt(an)_2(NO_2)_2]$, respectively, as follows: νNO_2 asym: 1418, 1406; νNO_2 sym: 1355, 1337 cm^{-1}; δNO_2: 831, 823 cm^{-1}; NO_2 wag: 610, 625 cm^{-1}. None of these bands exhibits a shift exceeding 1 cm^{-1} on d_5-labelling of aniline. The complete list of ligand bands is given in the reference.[22]

From Table VIII, it is observed that the νPt–X bands are recognized by complete absence of shift on ^{15}N- and d_5-labelling with the exception of νPt–I which shifts by 7 and 5 cm^{-1} for the *cis*- and *trans*-complexes, respectively, in the deuterated samples. In these cases, coincidence of νPt–I with δN–Pt–N causes the sensitivity towards deuteration. The two components of the νPt–X bands in the *cis*-complexes are only just resolved in the spectra of all of the complexes except for X = Br. In the spectra of the *trans*-complexes, they are true singlets. These observations conform with symmetry expectations (two νPt–N and two νPt–X bands anticipated for the C_{2v} *cis*-isomer and one of each for the D_{2h} *trans*-isomer). The ratios νPt–Br/νPt–Cl and νPt–

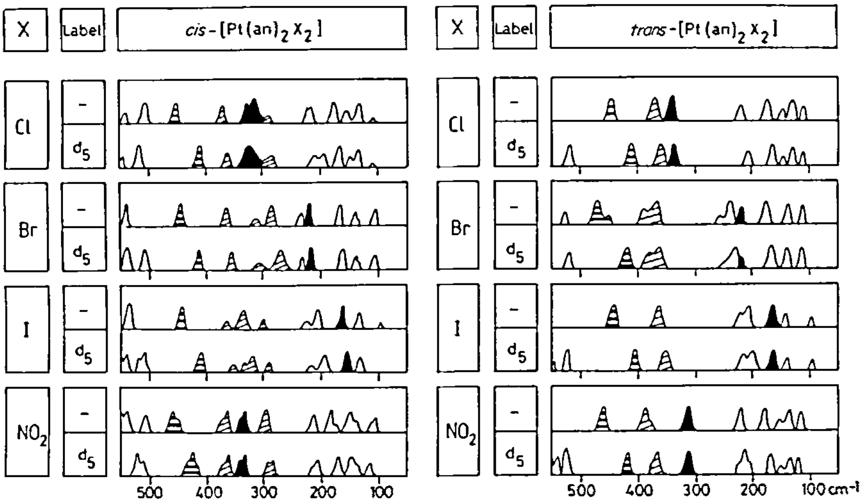


FIGURE 7 Far-infrared spectra of complexes [Pt(an)$_2$X$_2$]. Solid bands, νPt–X; shaded bands, νPt–an; bands with horizontal bars, NH_2 rock.

TABLE VIII
Far-infrared frequencies (cm^{-1}) for the complexes [Pt(an)$_2$X$_2$]

X = Cl (^{15}N-, d_5-shift)	X = Br (d_5-shift)	X = I (d_5-shift)	X = NO_2 (d_5-shift)	Assignment
cis-*[Pt(an)$_2$X$_2$]*				
451(5,41)	446(39)	439(36)	450(29)[a]	NH_2 rock
374(4,11)	367(12)	350(10)[a]	370(7)[a]	νPt–an
330[a](0,0)	223(0)	167(7)[b]	332(0)[a]	νPt–X
293(2,10)	290(10)[a]	300(10)	298(10)	νPt–an
220[a](0,12)	236(7)[a]	217(10)[a]	215(10)	γ ring
177(2,5)	171(5)	167(7)[c]	178(8)	δan–Pt–an
147(0.3)	141(1)	134(3)	144(2)[a]	δan–Pt–X
109(tb)[d]	107(0)	98(–)	105(0)	δX–Pt–X
trans-*[Pt(an)$_2$X$_2$]*				
449(5,38)	461(47)[a]	445(36)	458(40)	NH_2 rock
374(4,12)	383(12)[a]	366(10)	387(14)	νPt–an
340(0,0)	234(0)	168(5)[b]	312(0)	νPt–X
222(0,13)	240(12)	213(8)[a]	223(12)	γ ring
177(0,5)	177(6)	168(5)[c]	179(7)	δan–Pt–an
142(0,2)	140(0)	146(5)	148(4)[a]	δan–Pt–X
121(0,0)	114(0)	97(0)	117(0)	δX–Pt–X

[a] Mean of split peak.

[b] Coincident with δan–Pt–an.

[c] Coincident with νPt–X.

[d] Too broad for shift to be determined.

I/νPt–Cl are approximately 0.68 and 0.51, respectively. These are reasonable values in relation to those observed for the $[PtX_4]^{2-}$ ions.[23]

The νPt–N bands are readily recognized by their ^{15}N-shifts (2 to 4 cm^{-1} in the chloro complexes) and their d_5-sensitivities (7 to 14 cm^{-1}). In accordance with symmetry requirements, there are generally two bands in the *cis*-complexes and one in the *trans*-compounds. However, the *cis*- iodo and *cis*-nitro complexes show some further splitting and the νPt–N band of the *trans*-bromo compound is also split. The symmetry requirements of the aniline complexes are obeyed rather better than for their pyridine analogues.[24] In the complexes *cis*- and *trans*-$[Pt(py)_2X_2]$, two νPt–N bands are observed in the spectra of the former while *three* are seen for the *trans*-isomers.[24] However, of the three latter bands, two are sensitive to halogen substitution and are therefore assigned to coupled νPt–N + νPt–X bands. No such complications arise in the platinum(II) aniline complexes. Table IX shows a comparison between the two series.

TABLE IX

Comparison of the metal–ligand frequency data (cm^{-1}) for the complexes *cis*- and *trans*-$[PtL_2X_2]$ (L = an, py)

	$[Pt(an)_2X_2]$[22]			$[Pt(py)_2X_2]$[24]		
Band	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
cis-complexes						
νPt–N	374	367	350[a]	256	259	244
	293	290[a]	300	232	230	220
νPt–X	330[a]	223	167	345	216	175
				331	208	165
δN–Pt–N	177	171	(167)			
δN–Pt–X	147	141	134			
δX–Pt–X	109	107	98	160		
trans-complexes						
νPt–N	374	383	366	285	296	290
νPt–X	340	234	168	344	212	179
δN–Pt–N	177	177	(168)			
δN–Pt–X	142	140	146			
δX–Pt–X	121	114	97	165		

[a] Mean of split peak

The abovementioned study of the *cis*- and *trans*-isomers of $[Pt(an)_2X_2]$ was extended[25] to the complexes $[Pt(R\text{-}an)_2Cl_2]$ where R-an is a range of ten variously-substituted anilines comprising both electron-withdrawing and electron-releasing substituents, the extent of which was determined by their Hammett σ-values. The *cis*-bromo complexes were also examined. The assignments of one of the νPt–N bands could be made with reasonable certainty. The second νPt–N band in the *cis*-complexes was not always observed since it was overlaid by ligand bands. Two νPt–X bands were generally observed in the *cis*-complexes but as they comprised a band and shoulder or a nearly-coincident pair of bands, the mean frequency was taken for the purpose of determining the substituent effects.

TABLE X
νPt–N and νPt–X frequencies for complexes $[Pt(R\text{-}an)_2X_2]$

		cis- $[Pt(R\text{-}an)_2Cl_2]$		*cis*- $[Pt(R\text{-}an)_2Br_2]$		*trans*- $[Pt(R\text{-}an)_2Cl_2]$	
R	σ	νPt–N	νPt–Cl[a]	νPt–N	νPt–Br[a]	νPt–N	νPt–Cl
m-I	+0.35	390	341	381	222	396	335
p-I	+0.28	387	331	390	225		
m-OCH_3	+0.11	372	336	367	231	381	335
H	0	371	338	366	223	372	338
p-OC_6H_5	−0.03	384	336	380	223	384	335
p-C_2H_5	−0.15	360	335	365	225	359	334
p-n-C_4H_9	−0.16	383	330	388	226	394	335
p-CH_3	−0.17	373	333	372	219	350	321
3,4-di-CH_3	−0.24	355	334	365	224	352	333
p-OCH_3	−0.27	356[a]	329	352[a]	225	378	329

[a] Split peaks

The data in Table X show that the effect of electron-withdrawing substituents (positive σ) is to increase νPt–N but there is little effect on νPt–X. The abstraction of electron density from the Pt(II) ion is apparently not transmitted to the Pt–X bonds. A similar situation exists for the complexes *trans*-$[Pt(C_2H_4)(4\text{-}R\text{-}py)Cl_2]$ (where 4-R-py is a range of various 4-substituted pyridines) in which the substituents only affect the Pt–N bonding.[26] Unlike the situation for the aniline complexes discussed here, no regularity in the dependence of νPt–N on σ was observed for the pyridine complexes. The difference presumably arises because in the pyridine series, a particular substituent may induce opposing σ- and π-bonding influences between the Pt(II) ion and the pyridine ring. In the aniline complexes, no π-bonding is possible and the substituent influences only the Pt(II)-amine σ-bonding. Thus, a qualitative correlation exists between νPt–N and σ.

6. THE COMPLEXES $[M(R\text{-}an)_2X_2]$ (M = Mn, Co, Ni, Cu, Zn; R-an = substituted aniline; X = Cl, Br, I)

In view of the success which had attended the assignments of ligand and metal–ligand bands in the aniline complexes $[M(an)_2X_2]$ on the basis of ^{15}N-labelling and metal ion substitution studies,[9] these techniques were extended to the corresponding complexes of the methyl-substituted anilines: *o*-, *m*- and *p*-toluidine with the first transition series metal(II) ions: Co(II), Ni(II), Cu(II) and Zn(II).[27,28] In these three series of complexes, the Co(II) and Zn(II) complexes are tetrahedral, the Ni(II) complex is polymeric octahedral and the Cu(II) compound is polymeric tetragonal. Thus they are entirely isostructural with the corresponding complexes of aniline.

The earliest work on these compounds had been carried out by Ahuja *et al.*[29] in which assignments were made on a purely empirical basis. Because of the instrumental limitations of the period, several of the νM–N and νM–Cl bands were unassigned. The earliest attempt at making use of the isotopic labelling technique involved ^{15}N-labelling of *p*-toluidine in the complexes $[M(p\text{-}tol)_2Cl_2]$ (M = Co, Ni, Cu, Zn).[27]

This work was successful at assigning the νM–N bands which were observed at 426(Co), 414(Ni), 445(Cu) and 423(Zn) cm^{-1} but the second νM–N band was not always observed, nor could the νM–Cl bands be assigned with certainty, again because of instrumental limitations which prevented an examination of the effects of halogen substitution on the spectra.

Four years later, instrumental facilities in the relevant laboratory had improved to the extent that spectra down to $140\,\mathrm{cm}^{-1}$ were feasible and the effects of halogen substitution could be examined. Therefore a complete study[28] of the complexes $[\mathrm{ML_2X_2}]$ (M = Co, Ni, Cu, Zn; L = *o*- or *m*-toluidine; X = Cl, Br, I) was made over the range $4000–140\,\mathrm{cm}^{-1}$ with assignments based on ^{15}N-labelling and the effects of metal ion substitution.

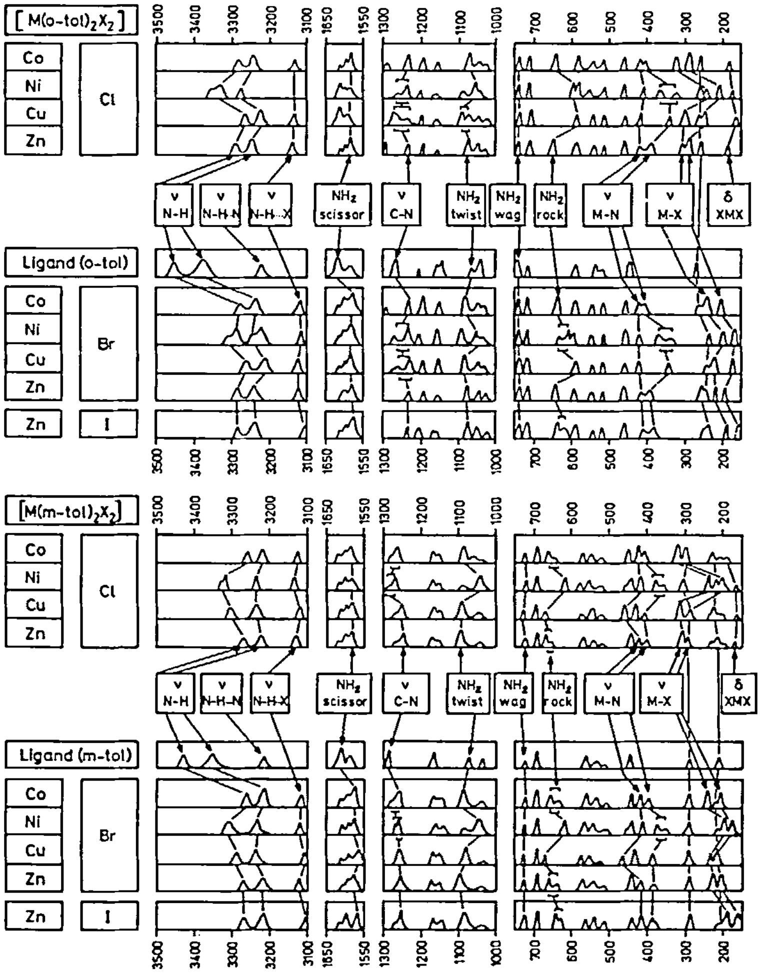


FIGURE 8 Infrared spectra of *o*- and *m*-toluidine complexes $[\mathrm{ML_2X_2}]$.

Assignment of the internal amino group vibrations were readily made on the basis of the ^{15}N-labelling technique, the results being similar to those discussed in Section 2 for the aniline complexes. The spectra are depicted in Fig. 8. Distinction between the νM–N and νM–X bands is readily made on the basis of the observed ^{15}N-shifts. Thus, the pair of νM–N bands in each complex shifts between 2 and 8 cm^{-1} on ^{15}N-labelling whereas the pair of νM–X bands is totally unaffected by the heavier isotope.

The νM–N and νM–X frequencies are listed in Table XI together with those resulting from the empirical study of Ahuja *et al.*[29] The principal difference is that many of the νM–Br and νM–I bands were near or below the low-frequency limit of measurement in the empirical study and were therefore not observed. Furthermore, the internal vibrations of the amino group were not assigned in the empirical study.

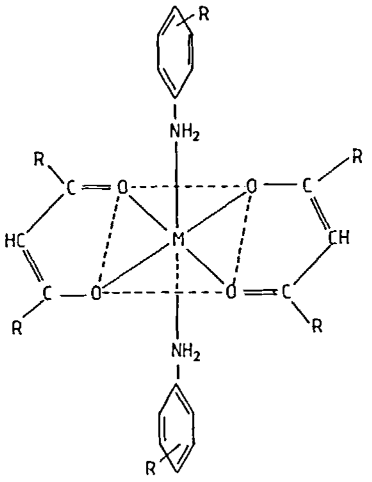


FIGURE 9 Formula of the complexes *trans*- [M(β-dik)$_2$(an)$_2$].

7. ANILINE AND SUBSTITUTED ANILINE ADDUCTS OF METAL β-KETOENOLATES, *trans*-[M(β-dik)$_2$(an)$_2$] and *trans*-[Co(acac)$_2$(an)(NO$_2$)]

These complexes of metal(II) ions have the formula shown in Fig. 9. Compounds of this type with the acetylacetonate (acac) anion as the β-ketoenolate and adducted aniline were first reported in 1969[30,31] although adducts with other bases had long been known. The ir spectra of a series of eleven of the Ni(II) complexes with various electron-withdrawing and electron-releasing substituents, R, in the aniline ring, have been examined down to 300 cm^{-1}.[32] Only νN–H and νNi–O modes could be assigned on an empirical basis. Relative to anhydrous [Ni(acac)$_2$]$_3$, an octahedral oligomer, the νNi–O bands were shifted to lower frequency by adduct formation. The νNi–O frequencies are also lower than those of *trans*-[Ni(acac)$_2$(H$_2$O)$_2$]. This was attributed to the higher ligand field strength of the amines which leads to stabilization of the Ni–N bonds at the expense of the Ni–O bonding. Introduction of electron-releasing substituents into the aniline ring further decreases the νNi–O frequencies. The νNi–O values were found to decrease by 8 cm^{-1} over the range $\sigma = +0.37$ (*m*-chloroaniline) to $\sigma = -0.27$ (*p*-methoxyaniline). Conversely the frequencies of the antisymmetric and symmetric νN–H modes *increased* by 18 and 10 cm^{-1}, respectively, over this range of substituents.

TABLE XI

Metal-ligand stretching frequencies of substituted aniline complexes $[M(R\text{-}an)_2X_2]$

			νM–N				νM–X				
R-an	M	X	^{15}N-labelling[a,28]		Empirical[29,h]		^{15}N-labelling[a,28]		Empirical[29]		
o-Toluidine	Mn	Cl			383				233		
	Co	Cl	418(4)	404(5)	418	396	328(0)	297(0)	325	292	
	Ni	Cl	408	344[b]	400	351	247	208	236		
	Cu	Cl	419(4)	345(3)	417	403[c]	302(0)	253(0)	336[d]	305	294[e]
	Zn	Cl	415(3)	396(6)	411	390	309(0)	294(0)	303	285	
	Co	Br	415(4)	402(4)	408	398	246(0)	202(0)	245		
	Ni	Br	413	353[b]	403	366	192	162			
	Cu	Br	419	340	416	400[c]	224	169	230		
	Zn	Br	412(2)	390(5)	404	385	227(0)	195(0)	250[e]		
	Co	I		405	388				256	247	
	Zn	I	410(2)	380(3)	405	377	191(0)	156(1)			
m-Toluidine	Mn	Cl							227		
	Co	Cl	429(2)	404(4)	424	400	323(0)	300(0)	320	298	
	Ni	Cl	423(2)	377(8)	417	349[c]	243(0)	208(0)	238		
	Cu	Cl	456(8)	410(8)	403		316(0)	287(0)	315	284	
	Zn	Cl	426(3)	396(4)	417	385	307(0)	296(0)	303		
	Co	Br	424(3)	402(4)	424	397	244(0)	211(0)	246		
	Ni	Br	418(2)	372(6)	413	349	196(0)	179(0)			
	Cu	Br	468(5)	393(3)	389		239(0)	220(0)	239		
	Zn	Br	417(4)	387(6)	411	382	227(0)	208(0)	232		
	Zn	I	412(2)	380(6)	408	370	189(0)	155(0)			
p-Toluidine[g]	Mn	Cl			397	370			227		
	Co	Cl	426(2)	400(3)[f]	420	396	326[f]	296(0)[f]	318	292	
	Ni	Cl	414(4)		405	386					
	Cu	Cl	445(8)		403	384	308(2)[f]		322	303	
	Zn	Cl	423(4)	399(2)[f]	417	395	311(0)[f]	299(0)[f]	298		

			vM–N			vM–X			
R-an	M	X	^{15}N-labelling[a,28]	Empirical[29,h]		^{15}N-labelling[a,28]	Empirical[29]		
3,4-Xylidine	Mn	Cl		366			233		
	Co	Cl		416	396		320	294	
	Ni	Cl		389			238		
	Cu	Cl		425	408		333	307	282
	Zn	Cl		413			307	294	
	Mn	Br					363		
	Co	Br		395			241		
	Ni	Br					392		
	Cu	Br		425	408		227		
	Zn	Br		408			227		
	Ni	I		386					
	Zn	I		416					
2,5-Xylidine	Co	Cl		400	387		325	296	
	Ni	Cl		347			224		
	Cu	Cl		412	384		335	303	294
	Zn	Cl		386			315	295	
	Co	Br		398	377		238		
	Ni	Br		400	352				
	Cu	Br		412	384		227		
	Zn	Br		380			227		
	Co	I		395					
	Zn	I		373					
2,6-Xylidine	Zn	Cl		390	357		315		
	Zn	Br		387	348		256		
	Zn	I		377	346				

[a] Figures in parentheses are the ^{15}N-shifts to lower frequency

[b] Mean of doublet

[c] Band not observed in ^{15}N-labelling study

[d] Assigned to vM–N in the ^{15}N-labelling study

[e] Assigned to a ligand mode in the ^{15}N-labelling study

[f] Assignment made subsequent to ref. 27

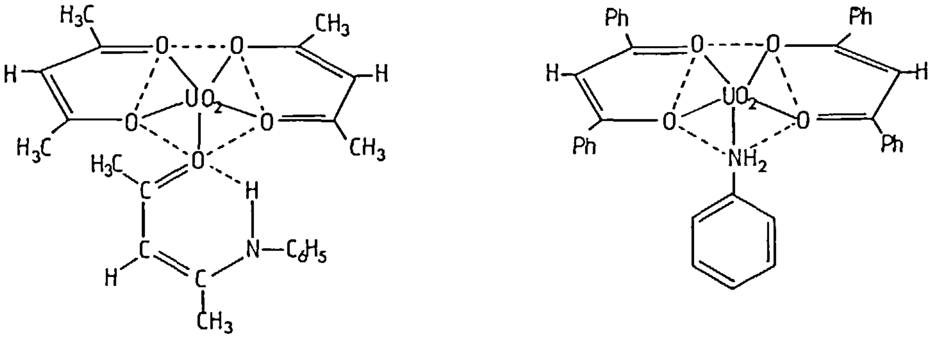
[g] ^{15}N-labelling data from ref. 27

[h] Described as 'other modes', probably vM–N[29]

In examining the reaction of amines with uranyl β-ketoenolates, Haigh and Thornton[33] found that $[UO_2(acac)_2]$ reacted with aniline to give the adduct $[UO_2(acac)_2(CH_3COCH{=}C(CH_3)NH{-}C_6H_5]$, *i.e.* *a* β-ketoimine adduct of uranyl acetylacetonate. The complex was shown by ^1H nmr and ir spectroscopy to have the structure shown in Fig. 10(a).

The ir spectrum showed a νC–O band of the adducted β-ketoimine molecule at 1615 cm^{-1} and νC–O of the chelated acetylacetonates at 1583 cm^{-1}. Likewise two νC–C bands were observed at 1551 and 1522 cm^{-1}. No νU–N band was observed.

By contrast, $[UO_2(dbm)_2(H_2O)]$ (dbm = dibenzoylmethanate) reacts with aniline to form a normal adduct formulated $[UO_2(dbm)_2(an)]$, Fig. 10(b). The ir spectrum of this complex[33] comprises only one chelated νC–O band at 1540 cm^{-1} and only one νC–C band at 1523 cm^{-1}. The νU–NH_2 band was observed at 516 cm^{-1}.



(a) (b)

FIGURE 10 (a) Structure of the product of the reaction of aniline with $[UO_2(acac)_2]$; (b) Structure of the product of the reaction of aniline with $[UO_2(dbm)_2(H_2O)]$.

In 1973, Fleming and Thornton[34,35] examined the ir spectra of a series of complexes of general formula *trans*-$[Co(acac)_2(R\text{-}an)(NO_2)]$ in which R-an represents eighteen variously substituted anilines. The structure of these complexes is depicted in Fig. 11.

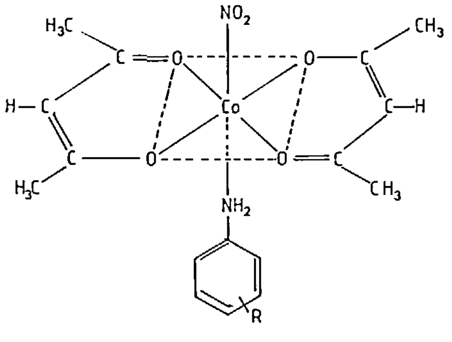


FIGURE 11 Structure of the complexes *trans*-$[Co(acac)_2(R\text{-}an)(NO_2)]$.

Assignments for the NH_2 modes, νC–N and νCo–N were made by ^{15}N-labelling of the complexes with R = H (aniline) and 4-CH_3 (*p*-toluidine). The νCo–NH_2 bands shifted by 6 and 10 cm^{-1}, respectively, on ^{15}N-labelling. The νCo–O bands were assigned on the basis of their zero shifts to peaks at 474 and 468 cm^{-1}, respectively, (they occur near these positions in the spectrum of [$Co(acac)_3$]). The νCo–NO_2 mode was assigned to bands near 435 and 360 cm^{-1} which were also not significantly sensitive to ^{15}N-labelling.

The partial spectra of the complexes are depicted in Fig. 12. The solid bands are those which shift by more than 2 cm^{-1} to lower frequency on ^{15}N-labelling. The spectra are placed in order of the Hammett σ-values of the substituents. *Ortho*-substituents have been excluded since they would be subject to steric effects on coordination. Because of the near band-for-band correspondence of the spectra, finding corresponding bands is a relatively simple matter.

The νCo–NH_2 bands are observed to move towards higher frequency with increased electron-releasing capacity of R. Since electron-releasing substituents will serve to increase the donor capacity of the amino groups, this is the expected direction for a band assigned to νCo–NH_2. The νCo–O bands were found to move in the opposite direction to νCo–NH_2. This indicates that increased strength of the Co–N bonds is accomplished at the expense of the Co–O bonding as had been observed for the amine adducts of nickel(II) acetylacetonate.[32]

The νCo–NO_2 bands move in the same direction as the νCo–O bands, *i.e.* stabilization of the Co–NH_2 bonds occurs at the expense of both the Co–O and the Co–NO_2 bonding.

8. THE COMPLEXES *trans*-[Pt(CH_2=CH_2)(R-an)X_2] (X = Cl, Br) and *trans*-[Pt(CO)(R-an)Br_2]

The vibrational spectra of Zeise's salt, K[Pt(CH_2=CH_2)Cl_3] and its derivatives *trans*-[Pt(CH_2=CH_2)(L)X_2] where L represents various oxygen- and nitrogen-donor ligands, have elicited much interest although only one study[26] had been reported for the complex with L = aniline and X = Cl prior to 1983 and this did not employ isotopic labelling as an assignment technique. Thus, the band at 346 cm^{-1} in the empirical study, assigned to νPt–N, was subsequently found to be unaffected by deuteration of aniline and therefore re-assigned to νPt–Cl. Isotopic labelling appears to be essential for distinguishing between the νPt–C_2, νPt–NH_2, νPt–X and νC=C bands which are present in these complex spectra and independent deuteration of ethylene (C_2D_4) and aniline (d_5) as well as the effects of halide substitution were successfully employed in 1983 to resolve the assignment problem in these complexes over the range 4000–80 cm^{-1}.[36] A corresponding study of the ^1H-nmr and uv spectra was also made.

Deuteration of ethylene causes the CH_2 stretching and bending modes and the C=C stretches to shift markedly towards lower frequency while d_5-deuteration of aniline leaves them completely unaffected. Conversely, deuteration of aniline leads to large shifts in the NH_2 modes and negligible shifts in the ethylene vibrations. The more specific distinctions between the C–H and ring modes of aniline were made on the basis of the ν^D/ν^H ratio using a value of 0.80 for this ratio to distinguish between the two types of aniline modes. The frequency data for the complexes with X = Cl are given in Table XII.

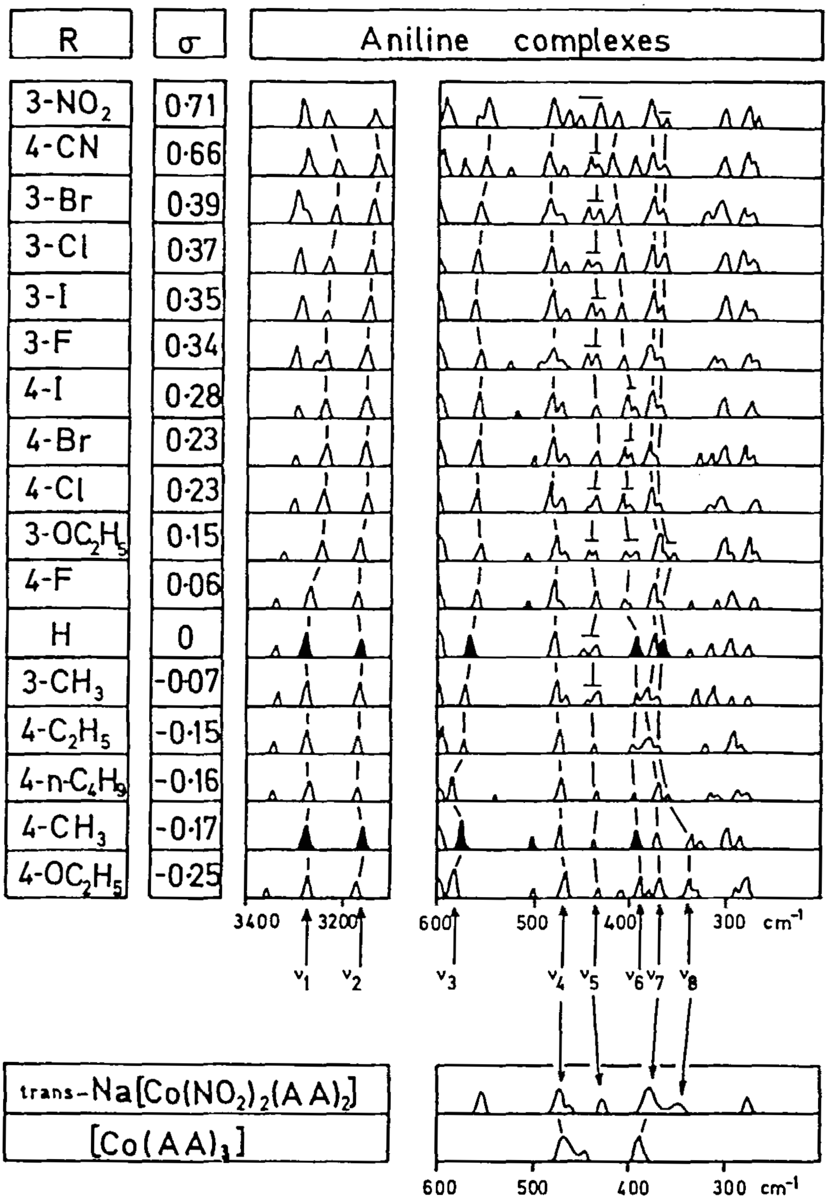


FIGURE 12 Infrared spectra of aniline complexes. Solid bands exhibit ^{15}N-shifts $> 2\,\mathrm{cm}^{-1}$. Assigned bands: ν_1:νN–H antisym; ν_2:νN–H sym; ν_3:νCo–N + NO_2 wag; ν_4:νCo–O; ν_5νCo–NO_2; ν_6:νCo–N + νCo–O; ν_7:νCo–O; ν_8:νCo–NO_2

The far-ir spectra for the normal and labelled species of the complexes with X = Cl, Br and depicted in Fig. 13. The work described above was further extended in 1983 and 1984 to variously substituted aniline complexes.[37,38] The data indicate (Table XIII) that electron-releasing substituents cause a simultaneous increase in

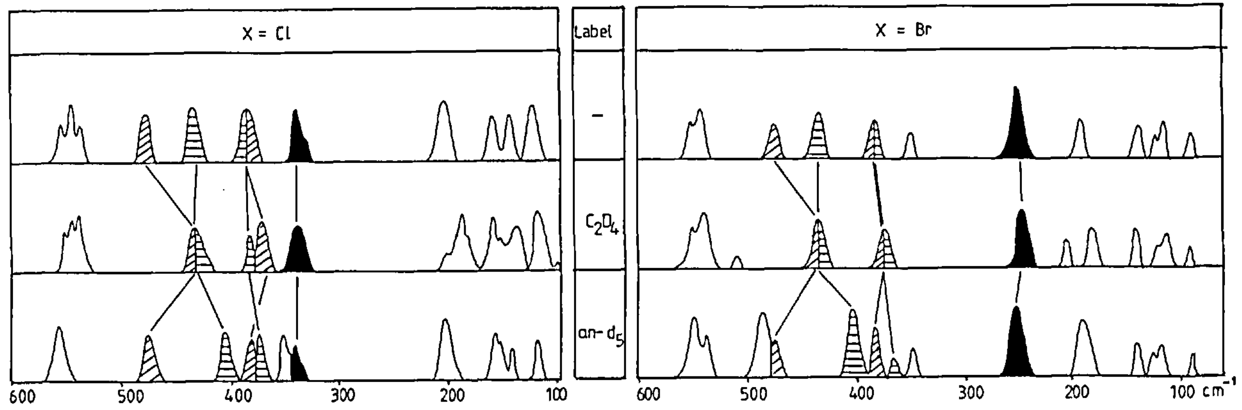


FIGURE 13 Far-ir spectra of *trans*-[Pt(CH_2=CH_2)(an)X_2].

TABLE XII
Mid-ir spectra of the complexes *trans*-[Pt(CH_2=CH_2)(an)Cl_2]

Band Frequency (cm^{-1})			
Unlabelled	C_2D_4-Labelled	an-d_5 Labelled	Assignment
3240	3236	3238	νN-H
3208	3202	3206	
3128	3124	3126	νN-H---Cl
	2362		νC-H(ethylene)
	2306		
	2222		
		2342	νC-H(aniline)
		2292	
		2284	
		2270	
1600	1597	1587	ν ring
1578	1577	1565^{a}	NH_2 scissor
1494	1491	1425	ν ring
1470^{a}	1469^{a}	1381	
1425	808	1425	CH_2 scissor
1255	959	1255	νC-C (ethylene)
		1160^{a}	ν ring
1161	1158	1132	+NH_2 twist
1068	1064^{a}	841	δC-H
1027	1025	820	
1014^{a}	684	1014^{a}	CH_2 wag
902	899	638	γC-H (an)
798	795	747	NH_2 wag
755^{a}	753^{a}	559	γC-H (an)
686	684	(559)	γ ring
554	552	(559)	NH_2 rock
543	541	499	δ ring
538	536	(499)	

[a] Mean of doublet

ν$Pt-C_2$, νPt-N and νC=C, suggesting that the electronic effects of the substituents are transmitted throughout the complex molecule. It is interesting to note that the mass effects of the substituents are apparently swamped by their electronic effects. Further extension of this work to the complexes *trans*-[Pt(CO)(R-an)Br_2] yielded similar results.[38]

9. DIANILINE-METAL(II) TETRACYANOMETALATE COMPLEXES

In a series of papers on clathrate and inclusion compounds, the Hofmann aniline clathrates $M(NH_3)_2Ni(CN)_4.2C_6H_5NH_2$ (M = Cd, Ni) were included for study.[39] The occurrence of a solid state ligand replacement reaction in which the aniline guest molecule replaces the coordinated ammonia to give $M(an)_2Ni(CN)_4$ as final product, was monitored by the time-dependent changes observed in the ir and Raman spectra of the clathrates.[40] The clathrates themselves are beyond the scope of this review but e products of the exchange reactions, the dianiline-metal(II) tetracyanometalates, mprise coordinated aniline in which bonding to the first transition series metal(II) ns Mn, Fe, Co, Ni and Cu occurs.

The ir spectra of the complexes of general formula $[M(an)_2M'(CN)_4]$ ($M' = Ni$, t) were examined down to 250 cm^{-1}.[41] It was observed that there is a correlation tween the shifts of certain aniline bands on coordination and the νM–N values hich were assigned to bands within the range 300–280 cm^{-1}. It was further bserved that, in accordance with the findings of Lever and Ramaswamy,[18] the equencies of the NH_2 wagging and rocking modes and the νM–N bands increased hen the temperature was decreased to 83 K. By contrast, the NH_2 stretching equencies decreased and the aniline ring and C–H modes were relatively insensitive decreased temperature.

TABLE XIII

rincipal far-ir bands for the complexes *trans*-$[PtL(R\text{-}an)X_2]$ ($L = CH_2{=}CH_2$, CO; X = Cl, Br) (cm^{-1})

.	σ	νPt–C_2		νPt–N	νC=C
= Cl; L = $CH_2{=}CH_2$[a]					
-NO_2	+0.78	430	372	394	1222
-NO_2	+0.71	437[e]	370	393	1222
-Br	+0.39	450[e]	381	395	1220
-Cl	+0.37	449[e]	383	403	1230[e]
-I	+0.35	446[e]	379	392	1235[e]
-F	+0.34	453	383	400	masked
-I	+0.28	451	380[e]	399	1222
-Br	+0.23	456	383	400	1226
I	0	476(45,0)[f]		434(3,30)[f]	1255
		384(15,3)[f]		384(2,11)[f]	
-OC_6H_5	−0.03	480	384	419	masked
-CH_3	−0.07	484	383	420	1253
-*t*-C_4H_9	−0.12	483	389	412	1257
-CH_3	−0.17	488	389[e]	420	1256[e]
,4-di-CH_3	−0.24	487	387	433	1252
-OCH_3	−0.27	498	390	426	1263sh
= Br; L = $CH_2{=}CH_2$[b]					
-NO_2	+0.71	420	353	374	1250
-Br	+0.39	459	377	393	1250
-Cl	+0.37	426	377	397	1251
-I	+0.35	462	373	421	1248
-F	+0.33	450	380	424	masked
-I	+0.28	450	353	404	1227
-Br	+0.23	461	360	408	1234
-Cl	+0.23	458	378	410	1249
n-OCH_3	+0.11	457	386	427	1250
I	0	477(42,0)[f]		434(0,31)[f]	1252
		384(9,2)		382(9,19)[f]	
n-CH_3	−0.07	480	378	431	1249
-C_2H_5	−0.15	486	391	453	1249
,5-di-CH_3	−0.16	483	384	443	1251
-*n*-C_4H_9	−0.16	484	390	440	masked

TABLE XIII (*continued*)

R	σ	νPt–C_2		νPt–N	νC=C
p-CH_3	−0.17	487	390	451	1254
p-OCH_3	−0.27	496	386	485	masked
					$\overline{\nu C\equiv O}$[d]
X = Br; L = CO[c]					
m-NO_2	+0.71	495	473	355	2127.8
m-Br	+0.39	506	475	368	2126.5
m-Cl	+0.37	511	477	377	2126.4
m-I	+0.35	504	491	359	2126.3
m-F	+0.33	515	486	422	2126.5
p-I	+0.28	518	483	363	2126.1
p-Br	+0.23	512	486	369	2126.3
p-Cl	+0.23	527	483	388	2126.6
m-OCH_3	+0.11	526	490	428	2125.5
H	0	530(3)[g]		434(3)[g]	2125.5
		493(2)[g]		345(10)[g]	2125.5
m-CH_3	−0.07	532	506	460	2124.8
p-C_2H_5	−0.15	533	501	465	2124.5
3,5-di-CH_3	−0.16	533	505	469	2124.9
p-n-C_4H_9	−0.16	539	513	468	2124.7
p-CH_3	−0.17	530	506	476	2124.9
p-OCH_3	−0.27	542	508	477	2124.6

[a] νPt–Cl near 335 cm^{-1}; insensitive to R.

[b] νPt–Br near 244 cm^{-1}; insensitive to R.

[c] νPt–Br near 253 cm^{-1}; insensitive to R.

[d] νC≡O determined in $CHCl_3$ solution; all other frequency data from nujol mull spectra.

[e] Mean of doublet

[f] Figures in parentheses are the shifts to lower frequency on C_2D_4 labelling (first figure) and an-d_5 labelling (second figure)

[g] Figure in parentheses is the shift to lower frequency on an-d_5 labelling.

10. *TETRAKIS*- AND *HEXAKIS*(ANILINE) COMPLEXES OF RUTHENIUM(II) HALIDES

These complexes are of interest because they involve a rare example of six aniline molecules octahedrally coordinated around a metal(II) ion. With metal(II) ions, not more than four aniline molecules have formerly been successfully accommodated around the ion. In 1971, Larkworthy and co-workers[42] unsuccessfully attempted to obtain aniline complexes of Ru(III) by direct reaction between aniline and $RuCl_3$. However, oxalato complexes of the type $K[Ru(oxalate)_2(aniline)_2]$, when treated with concentrated halogen acids followed by further aniline, led to reduction and the formation of tetra- and hexa-aniline complexes of Ru(II) such as $[Ru(an)_4Br_2]$ and $[Ru(an)_6]Br_2$. A band near 235 cm^{-1} in the Ru(III) oxalate–aniline complex was found to be insensitive to halide substitution and was therefore tentatively assigned to νRu^{III}–N. No assignments of the νRu^{II}–N modes were made although the band at 371 cm^{-1} seems a likely candidate. Clearly, a detailed vibrational study of these molecules would be of great interest.

KNOWLEDGEMENTS

wish to thank the publishers for permission to reproduce Figures and Tables as llows: Pergamon Press for Figs. 1 and 3 and Tables I and II (from ref. 6); Elsevier ıblishing Co. for Figs. 4 and 5 and Table V (from ref. 9); Fig. 6 and Table VI (from f. 19); Fig. 7 and Table VIII (from ref. 22); Fig. 8 (from ref. 28); Fig. 12 (from ref.) and Fig. 13 (from ref. 36); Marcel Dekker Inc. for Table X (from ref. 25).

FERENCES

K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 4th Edition, Wiley-Interscience, New York, 1986.
D.M. Adams, "Metal-Ligand and Related Vibrations", Arnold, London, 1967 p. 279.
J.R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum, New York, 1971 p. 198.
M.A.J Jungbauer and C Curran, *Spectrochim. Acta*, **21**, 641 (1965).
I.S. Ahuja, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1105 (1965).
A.T. Hutton and D.A. Thornton, *Spectrochim. Acta*, **34A**, 645 (1978).
J.C. Evans, *Spectrochim. Acta*, **16**, 438 (1960).
G.A. Foulds, J.B. Hodgson, A.T. Hutton, M.L. Niven, G.C. Percy, P.E. Rutherford and D.A. Thornton, *Spectrosc. Lett.*, **12**, 25 (1979).
J.A. Lee Thorp, J.E. Rüede and D.A. Thornton, *J. Mol. Struct.*, **50**, 65 (1978).
M. Goldstein and R.J. Hughes, *Inorg. Chim. Acta*, **40**, 229 (1980).
M. Goldstein and W.D. Unsworth, *J. Mol. Struct.*, **14**, 451 (1972).
M. Noji and Y. Kidani, *Bunseki Kagaku*, **24**, 545 (1975).
S. Akyüz and J.E.D. Davies, *J. Mol. Struct.*, **95**, 157 (1982).
I.S. Ahuja and P. Rastogi, *J. Inorg. Nucl. Chem.*, **32**, 2085 (1970).
L.G. Hulett and D.A. Thornton, *J. Inorg. Nucl. Chem.*, **35**, 2661 (1973).
L.G. Hulett and D.A. Thornton, *Spectrochim. Acta*, **29A**, 757 (1973).
D.A. Thornton, *Coord. Chem. Rev.*, **55**, 113 (1984).
A.B.P. Lever and B.S. Ramaswamy, *Can. J. Chem.*, **51**, 1582 (1973).
C. Engelter and D.A. Thornton, *J. Mol. Struct.*, **33**, 119 (1976).
J.E. Rüede and D.A. Thornton, *J. Mol. Struct.*, **34**, 75 (1976).
B.N. Figgis, "Introduction to Ligand Fields", Interscience, New York, 1966, p. 244.
T.P.E. Auf der Heyde, G.A. Foulds, D.A. Thornton and G.M. Watkins, *J. Mol. Struct.*, **77**, 19 (1981).
Ref. 3, p. 181.
C. Engelter, A.T. Hutton and D.A. Thornton, *J. Mol. Struct.*, **44**, 23 (1978).
T.P.E. Auf der Heyde, G.A. Foulds, D.A. Thornton and G.M. Watkins, *Spectrosc. Lett.*, **14**, 455, (1981).
M.A.M. Meester, D.J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, **14**, 25 (1975).
P.R. Johnson and D.A. Thornton, *Chimia*, **28**, 345 (1974).
C. Engelter, D.A. Thornton and M.R. Ziman, *J. Mol. Struct.*, **49**, 7 (1978).
I.S. Ahuja, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1625 (1965).
N.P. Slabbert and D.A. Thornton, *Inorg. Nucl. Chem. Lett.*, **5**, 921 (1969).
J.M. Haigh, N.P. Slabbert and D.A. Thornton, *J. Inorg. Nucl. Chem.*, **32**, 3635 (1970).
J.M. Haigh, N.P. Slabbert and D.A. Thornton, *J. Mol. Struct.*, **7**, 199 (1971).
J.M. Haigh and D.A. Thornton, *J. Inorg. Nucl. Chem.*, **33**, 1787 (1971).
C.A. Fleming and D.A. Thornton, *Spectrosc. Lett.*, **6**, 245 (1973).
C.A. Fleming and D.A. Thornton, *J. Mol. Struct.*, **27**, 335 (1975).
T.P.E. Auf der Heyde, G.A. Foulds, D.A. Thornton, H.O. Desseyn and B.J. van der Veken, *J. Mol. Struct.*, **98**, 11 (1983).
G.A. Foulds and D.A. Thornton, *J. Mol. Struct.*, **98**, 309 (1983).
G.A. Foulds, P.S. Hall and D.A. Thornton, *J. Mol. Struct.*, **117**, 95 (1984).
S. Akyüz, A.B. Dempster and R.L. Morehouse, *Spectrochim. Acta*, **30A**, 1989 (1974).
S. Akyüz, A.B. Dempster, J.E.D. Davies and K.T. Holmes, *J. Mol. Struct.*, **38**, 43 (1977).
S. Akyüz, *J. Mol. Struct.*, **68**, 41 (1980).
D.L. Key, L.F. Larkworthy and J.E. Salmon, *J. Chem. Soc., A*, 2583 (1971).