$Pt(II)[(2,2'\text{-}bpy)(NCO)_2]$ (2,2'-bpy = 2,2'-bipyridyl): an X-ray structure, NMR and FT-IR determination of pseudohalide bonding

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Abstract

A new synthetic procedure has been developed to obtain single crystals of the square planar complex $Pt(II)[2,2'\text{-}bpy)(NCO)_2]$ in which the two pseudohalide ligands occupy *cis* positions. The results of a complete X-ray diffraction study are reported, and confirm the N-bonding of the cyanate moiety in the solid. Both solid and solution infrared data are reported for this complex, in particular the characteristic signature of the NCO ligand. The relationship between the spectroscopic and structural data is discussed in detail. In addition, ^{13}C NMR data are reported for this complex in *N*-methyl pyrrolidone, and confirm the persistence of N-bonding of the NCO group in solution.

Introduction

The square planar d^8 metal complexes of group VIII (10) are interesting for a variety of reasons, including the prevalence of metal–metal bonding [1] in the solid state due to stacking of the (nearly) flat molecular units by utilizing d_z2 overlap, their potential as polyatomic intercalating moeities [2], the ubiquitous existence of polymorphism (especially as related to the observed reversible color changes reported for these complexes [3]), as well as their obvious relationship to the antitumor active cis-platin complexes [4]. It is thus surprising that despite the voluminous literature on Pt(II) pseudohalide complexes [5], very few crystallographic studies of these compounds have been published. Structural inferences related to the mode of pseudohalide ligation have been largely based on infrared evidence [6–8], but the conclusions drawn from such studies are frequently less than completely convincing. The majority of the transition metal cyanates which have been reported have been described in terms of metal–nitrogen ligation [9a, 10], but bonding of the cyanate via the oxygen atom was originally assumed to occur in a number of bis-cyclopentadienyl complexes by Burmeister *et al.* [7a]. In a subsequent dipole moment and infrared study [7b], it was concluded that the titanocene cyanate most likely contains N-bonded ligands, whereas the zirconocene cyanate is most likely O-bonded (see, however, Norbury [11]). Linkage isomerism in $Rh(PPhen_3)_3$'NCO' was first reported by Anderson and Norbury [11] in 1974. These authors made use of infrared absorbance data to distinguish between a yellow (–NCO) and orange (–OCN) reaction product, but pointed out the caution required to assign structures purely on the basis of spectroscopic evidence. Similar caveats concerning inferences relating to the pseudohalide bonding mode in octahedral hexa-cyanato complexes of Re and Mo have been raised by Bailey and Kozak [8]. In addition, it has become evident from the available experimental data, that while nickel thiocyanate complexes show N-bonding of the pseudohalide ligands, palladium complexes show both N-bonding and S-bonding [9b], while platinum (Pt(II)) complexes appear to show only S-bonding of this moiety. Whether similar systematics apply in the case of the NCO ligand is still an open question.

In an effort to relate the IR and NMR (^1H and ^{13}C) spectroscopic signatures of *cis* square planar Pt(II) complexes to a detailed crystal structure, an integrated study was undertaken to this end in which the several experimentally accessible techniques are focussed on a well characterized exemplar of such a pseudohalide complex, and the results of this effort are reported herein.

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Experimental

Synthesis of Pt[(2,2'-bpy)(NCO)$_2$]

Method a. Commercial (Aldrich) $K_2Pt(Cl)_4$ was converted to Pt(bpy)$(Cl)_2$ by literature methods [6, 12, 4]. A total of 0.1036 g (0.245 mmol) of this complex was dissolved in ~15 ml dmso with slight warming. To this was added twice the stoichiometric amount (0.1016 g, 0.490 mmol) of $AgClO_4$ dissolved in 2 ml H_2O, which caused the immediate formation of AgCl in the bright yellow solution. The reactants were stirred for ~1 h while held at 75 °C and then filtered through an F-grade frit. The filtrate, to which a small amount of water was added to avoid sodification, was cooled to 0 °C, and to this was added slowly a slightly less than stoichiometric quantity of aqueous KOCN. The clear yellow solution was allowed to stand at room temperature for several days, after which the product was obtained as indigo–blue colored needles. These were removed by filtration, washed with EtOH and Et_2O, and vacuum dried at room temperature, Anal. found: C, 33.08; H, 1.67; N, 12.77. Calc. for $Pt_{12}H_8N_4O_2$: C, 33.11; H, 1.85; N, 12.87%.

Method b. A weighed quantity of Pt(bpy)$(Cl)_2$ was dissolved in dmso with slight warming. To this was added a stoichiometric amount of aqueous KOCN directly. The indigo–blue product crystals formed after standing for several weeks at room temperature. The product was washed and dried as above.

The two products gave identical IR spectra. The crystal chosen for the X-ray study was produced by method b.

VTFT-IR spectroscopy

The infrared spectra were acquired using a Mattson Cygnus-100 spectrometer (DTGS or MCT detector with KBr optics) at room temperature. The low temperature data were obtained using an IBM Model 32 spectrometer (DTGS detector, KBr optics) as described previously [13].

Nuclear magnetic resonance spectroscopy

The ^{13}C NMR data acquired in this study were obtained with natural abundance samples, using a 200 MHz Varian Model XL spectrometer. It should be noted that although the neat solid is composed of indigo colored crystals, the resulting solutions are orange–yellow. Solutions of the sample compound (*c* 1 ml) were prepared from saturated solutions in *N*-methyl pyrrolidone, filtered to remove solids, and examined at 295 K, using a 2 s delay time between pulses due to the slow relaxation of the pseudohalide C atom. The total number of pulses co-added was in excess of 60 k. Dmso in a sealed capillary introduced into the NMR tube, was used as an internal and scale reference.

X-ray diffraction studies

A large number of crystals, many of them twinned, were examined for crystallographic suitability. An indigo-colored needle shaped crystal was selected, cut and mounted for data collection. Data were obtained on a PW1100/20 Philips four-circle computer-controlled diffractometer. Mo Kα($\lambda = 0.71069$ Å) radiation with a graphite crystal monochrometer in the incident beam was utilized in data collection. The unit cell dimensions were obtained by a least-squares fit of 22 centered reflections in the range of $10 < \theta < 13°$. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan\theta$ with a scan speed of 3.0°/min. The profiles of a number of peaks were scanned and showed a singlet shape with a full width of less than 0.8°. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Reflections with $F < 6\sigma_F$ were considered unobserved and were rejected from the refinement process.

Intensities were corrected for Lorentz, polarization and absorption effects (based on the Ψ scans of two reflections). All non-hydrogen atoms were found by using the results of the SHELX-86 direct method analysis. Refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. A final dif-

TABLE 1. Crystal and refinement data for Pt[(2,2'-bpy)(NCO)$_2$][a]

Formula	Pt$(C_{10}H_8N_2)(NCO)_2$
Formula weight	435.31
Space group	$P3_121$
a (Å)	10.436(5)
c (Å)	9.688(5)
V (Å^3)	913.8(8)
Z	3
ρ_{calc} (g cm^{-3})	2.37
μ (Mo Kα) (cm^{-1})	110.65
No. unique reflections	630
No. reflections with $F \geqslant 6\sigma_F$	482
R[b]	0.056
R_w[b]	0.076
w	σ_F^{-2}
Temperature (K)	294(1)

[a] Non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis, [14]. All crystallographic computing was done on a Cyber 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

ference Fourier synthesis map showed several peaks less than 1.4 e Å^{-3} scattered about the unit cell without any significant feature. There are two large peaks (1.4 e Å^{-3}) very close to the Pt atom, while the rest of the peaks are less than 0.9 e Å^{-3}. The minimum peak is -1.3 e Å^{-3}. The goodness of fit is 4.2. This high value is a consequence of the tendency of the crystals to twin and/or a poor absorption correction – the best candidate of a large number examined was ultimately chosen for data collection and refinement. The large *GOF* is, of course, also reflected in the large e.s.d.s. reported. Despite these drawbacks, the crystallographic data provide convincing support for the interpretation of the spectroscopic results, and lead to a detailed understanding of the properties of the title compounds.

The discrepancy indices $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o \pm$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 1.

Results and discussion

Description of the structure

The structure of the title compound consists of neutral *cis*-Pt(II)[(bpy)(NCO)$_2$] molecules with the expected square-planar arrangement of the four ligand nitrogen atoms around the central metal which is located on a two-fold axis. The Pt–Pt intermolecular distances average 3.2350(5) Å. An ORTEP representation of the title compound, showing the atomic numbering scheme, is shown in Fig. 1.

The displacements from a least-squares plane of the four atoms making up the nearest neighbor environment around the metal center are N(1), 0.016; N(1′), −0.016; N(2), −0.013; N(2′), 0.013 Å. This defines plane No. 1. Each pyridine ring (plane No. 3) is nearly planar, with the C(1), C(3), C(4) and N(1) atoms slightly above the ring plane, and the C(2) and C(5) atoms displaced slightly below. The average deviation from the least-squares plane of the two six-membered rings (calculated by Hamilton's method) is 0.016 Å. This ring moiety including the platinum atom (plane No. 2) has a similar geometry, with N(1), C(5) and N(1′) slightly above the ring plane, and the metal atom and C(5′) slightly below. The dihedral angles are 1,52, 1.30 and 1.77°, respectively, between planes No. 1 and 2, planes No. 1 and 3, and planes No. 2 and 3, thus showing a flat molecular configuration around the metal atom.

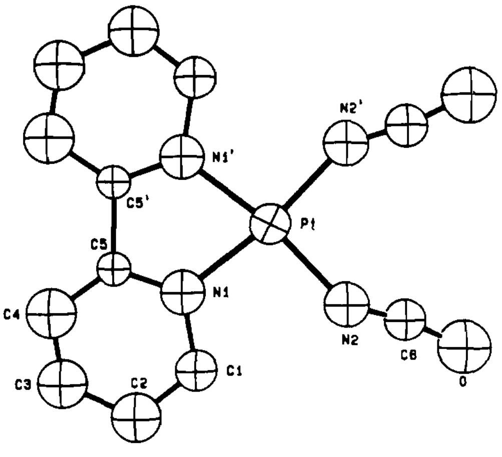

Fig. 1. ORTEP drawing of Pt[(2,2′-bpy)(NCO)$_2$] showing the atomic numbering scheme.

The correct choice of enantiomer is based on the observation that an interchange of coordinates (*x*, *y*, *z*, to $-x$, $-y$, $-z$) led to significantly poorer *R* factors ($R = 0.114$, $R_w = 0.163$) in the refinement.

The structural parameters of the bidentage ligand in the title compound are very similar to those reported very recently for Pt(bpy)(CN)$_2$ by Che *et al.* [15]. In the cyanate, the average C–C bond distance is 1.39(5) while in the cyanide, this value is 1.38(2). The C–N bond distances in the bpy rings average 1.38(7) and 1.32(1), respectively. There are no statistically significant differences in the N–C–C bond angle of the five-membered rings, but the Pt–N–C bond angles, differ somewhat, being 122(3) and 111.3(9)°, respectively. It is interesting to note that the bond distance between the Pt atom and the nitrogen of the bpy ligand is identical in the two compounds (1.99(2) and 2.00(1), respectively) despite the obvious fact that in the former, the N atoms is *trans* to the N atom of the pseudohalide, whereas in the latter the atom is the C atom of the cyanide.

An interesting feature of this structure is the bond angle of 147(5)° of the Pt–N(2)–C(6) portion of the molecule. For N-bonded thiocyanates, the reported [16, 17] metal–nitrogen–carbon bond angles generally have values vetween 150 and 180° (range 129–180°), whereas for S-bonded thiocyanates, the metal–sulfur–carbon bond angles are normally in the range $90 < \theta < 140°$. Since the cyanate ligand of the present structure is potentially able to ligate with either end to the metal atom, a refinement of the structure assuming O-metal bonding was also effected. Due to the presence of the heavy metal atom, and the nearly identical X-ray scattering factors for O and N, it is difficult to decide with confidence between the two possibilities solely on the basis of the calculated *R* factors [18]. Moreover, the isotropic thermal factors calculated for the two possible ligation modes, which are summarized in Table 2, are almost identical within the statistical significance criteria of the refinement. On the other hand, the bond lengths

TABLE 2. Isotropic thermal factors

Atom Refinement	Pt	N(2)	C(6)	O	*R*	R_w
PtNCO	0.0533(7)	0.068(9)	0.058(9)	0.097(9)	0.056	0.076
PtOCN	0.0533(7)	0.071(8)	0.061(9)	0.096(10)	0.058	0.077

TABLE 3. Representative NCO bond angles (in increasing order) and CN bond distances of transition metal cyanates

Compound[a]	Metal	M−N−C (°)	N−C (Å)	Reference
$Mn[TPP(NCO)_2]\cdot(C_7H_8)_{1/2}$	Mn(IV)	133.1(3) 136.5(3)	1.164(5) 1.171(5)	20
$Au[PPh_3(NCO)]$	Au(I)	142.6(6)	1.147(8)	21
$Pt[(C_3H_5NO)(Cl)(NCO)(tmen)$	Pt(II)	147(1)	1.11(2)	19
$Cu[(C_5H_5N)_2(NCO)_2]$	Cu(II)	151.83(61)[b]	1.152(10)[b]	22
$\{Ni[(tren)_2(NCO)_2]\}^{2+}$	Ni(II)	155.0(6)[b]	1.128(10)[b]	23
$\{Mn[(tren)_2(NCO)_2]\}^{2+}$	Mn(II)	158.3(5)[b]	1.157(8)[b]	24
$\{Cu[(tren)_2(NCO)_2]\}(BPh_4)_2$	Cu(II)	160(1)[b]	1.19(2)[b]	25
$Cu[(NCO)_2(terpy)]$	Co(II)	160.9(8)	1.126(9)	26
$Cu_4[(Et_2NC_2H_5O)(NCO)]_4$	Cu(II)	161.1(11)	1.100(15)	27
$Cu[(C_{11}H_{18}N_4O_2BF_2)(NCO)]$	Cu(II)	165.1(6)	1.133(10)	28
$[Ru(14\text{-}TMC)(NCO)O]ClO_4$	Ru(IV)	165.9(6)	1.154(10)	29
$[(CH_3)_4N]Ag(NCO)_2$	Ag(I)	171.1(12) 170.0(13)	1.111(18) 1.076(19)	30
$Ti[(cpd)_2(NCO)_2]$	Ti(IV)	171.8(3) 175.7(3)	1.151(5)	31
$Zr[(cpd)_2(NCO)_2]$	Zr(IV)	172.6(3) 177.5(3)	1.140(5)	31
$Mo[(cpd)(CO)(PPh_3)_2(NCO)]$	Mo(II)	173.3(9)	1.118(14)	32
$Cr[(cpd)(NO)_2(NCO)]$	Cr(IV)	180.0(4)	1.126(5)	33

[a] TPP = 5, 10, 15, 20-tetraphenyl porphinato; tmen = *N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine; tren = 2,2′,2″-triamino triethylamine; terpy = 2,2′,6′,2″-terpyridyl; 14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraaza cyclohexadecane; cpd = π-cyclopentadienyl. [b] Bridging pseudohalide group.

calculated for a structure involving an N-bonded configuration gave somewhat unrealistic values (Pt−O−C−N: 1.99, 1.17, 1.20 Å). Thus, despite the marginally better refinement favoring N-metal (rather than O-metal) ligation of the pseudohalide ligand, an unambiguous decision cannot be made solely on the basis of the X-ray crystallographic data, and additional spectroscopic evidence (*vide infra*) has to be marshalled in order to settle the question of the pseudohalide bonding to the metal atom. In this context, it is worth noting, however, that the single reported structure involving a Pt(II) cyanate link, as determined by Maresca *et al.* [19], was refined to yield essentially the same Pt−N−C bond angle (147(1)) and N−C bond distance (1.11(2)) as obtained in the present study. The results of a computer search of reported transition metal cyanates are summarized in Table 3, from which it is clear that a wide range of metal −N−C bond angles have been reported. All of these structures have been refined assuming N-bonding of the pseudohalide ligand. The observed bond distance of the CN portion of this ligand (1.13(6) Å) falls toward the short end of the reported range, but is identical to the corresponding

TABLE 4. Fractional atomic coordinates for $Pt[(2,2'\text{-}bpy)(NCO)_2]$[a]

Atom	*x*	*y*	*z*
Pt	−0.0106(1)	0.0000	0.3333
N(1)	0.207(3)	0.135(3)	0.327(3)
C(1)	0.264(4)	0.293(4)	0.320(3)
C(2)	0.414(5)	0.387(4)	0.317(3)
C(3)	0.507(4)	0.318(4)	0.315(4)
C(4)	0.453(5)	0.175(5)	0.323(4)
C(5)	0.301(3)	0.087(3)	0.323(3)
N(2)	−0.060(4)	0.162(4)	0.329(3)
C(6)	−0.145(4)	0.195(4)	0.303(3)
O	−0.220(3)	0.252(3)	0.277(3)

[a] e.s.d.s. in the least-significant digit are shown in parentheses.

TABLE 5. Selected bond distance (Å) and bond angles (°) for Pt[(2,2'-bpy)$(NCO)_2$]

Pt–N(1)	1.99(2)	C(3)–C(4)	1.31(6)
Pt–N(2)	2.00(5)	C(4)–C(5)	1.39(5)
N(1)–C(1)	1.44(5)	C(5)–C(5′)	1.57(4)
N(1)–C(5)	1.31(5)	N(2)–C(6)	1.13(6)
C(1)–C(2)	1.38(5)	C(6)–O	1.23(6)
C(2)–C(3)	1.46(8)		
N(1)–Pt–N(2)	95(2)	C(1)–C(2)–C(3)	117(5)
N(1)–Pt–N(1′)	76(2)	C(2)–C(3)–C(4)	123(6)
N(1)–Pt–N(2′)	171(1)	C(3)–C(4)–C(5)	117(4)
N(2)–Pt–N(2′)	94(2)	N(1)–C(5)–C(4)	125(4)
Pt–N(1)–C(1)	119(2)	N(1)–C(5)–C(5,b7)	110(4)
Pt–N(1)–C(5)	122(3)	C(4)–C(5)–C(5′)	125(3)
C(1)–N(1)–C(5)	119(4)	Pt–N(2)–C(6)	147(5)
N(1)–C(1)–C(2)	119(3)	N(2)–C(6)–O	170(6)

distance reported by Che *et al.* [34] for the tetracyano complex $Pt_2(dppm)_2(CN)_4$, while slightly longer than that reported by Che *et al.* [15] for the Pt(bpy)$(CN)_2$ complex referred to above. The bond order of the CN portion of the NCO group is thus similar to that in transition metal cyanides, consistent with the νCN values observed in the IR spectra.

The fractional atomic coordinates for the title compound are summarized in Table 4, and values for selected bond distances and bond angles are given in Table 5. See also Supplementary Material.

Infrared spectroscopy

The infrared spectra of metal-bonded pseudohalides have received considerable attention in the literature, and majore reviews which should be consulted are those by Norbury [35], Bailey *et al.* [36] and Nakamoto [37]. In an early detailed study of the NCO^- ion in alkali halide matrices, Maki and Decius [38] assigned the three fundamental modes of $^{14}N^{12}C^{16}O^-$ in KBr at 635.62 cm^{-1} for the bending mode, 1258.55 cm^- for the CO symmetric stretch, and at 2215.7 cm^{-1} for the CN stretch. The corresponding Raman data are given by Ti *et al.* [39]. For N-bonded cyanate complexes, Nakamoto [37] locates the three IR absorbance regions as 595–667, 1340–1482 and 2155–2284 cm^{-1}, respectively. Norbury and Sinha [6] reported the preparation of Pt(bpy)$(NCO)_2$ (which they characterized as 'black') and list the three absorbances at 576(m, sh), 1340(m, sh) and 2215–2225(s, with a shoulder at 2240) cm^{-1}, respectively. These authors also report the CN stretch for a sample in nitromethane at 2256 (no resolved splitting) with a half-width of 75 cm^{-1}. They assumed an essentially linear M–N–C bond with the negative charge localized primarily on the nitrogen atom of the pseudohalide ligand.

The results of the infrared measurements of the present study, together with relevant data for related compounds, are summarized in Table 6, and a typical trace of the CN stretching mode absorption is shown in Fig. 2, which shows the absorption profile of this band in a KBr matrix (both at 295 and 82 K), and in NMP (*N*-methyl pyrrolidone) solution. The latter

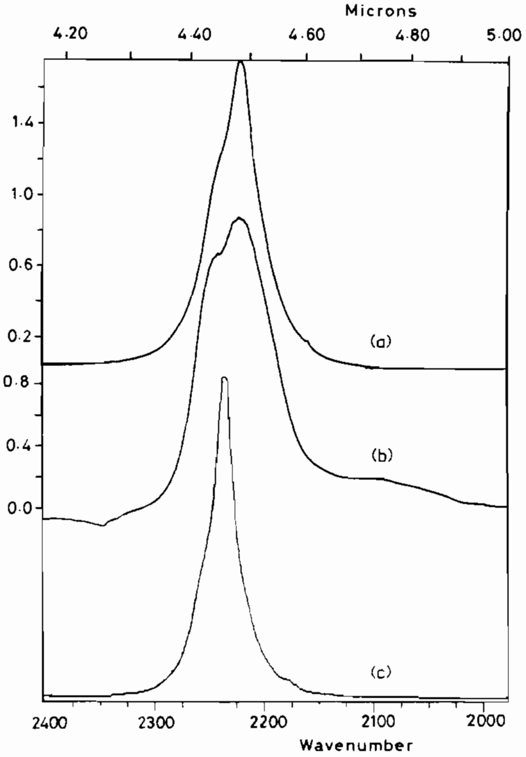

Fig. 2. CN stretching mode region of the IR spectrum of Pt[(2,2'-bpy)$(NCO)_2$]: (a) KBr pellet at 295 K, (c) KBr pellet at 80 K, (b) solution in *N*-methyl pyrrolidone at 295 K. For spectrum (b), the solvent blank has been subtracted. All three spectra show the presence of an (unresolved) pair of absorption bands, corresponding to the IR allowed symmetric and asymmetric stretching modes of the pseudohalide ligand.

TABLE 6. Cyanate group frequencies for the title compound and related species

Compound	Form	Temperature (K)	ν(CN) (cm^{1})	ν(CO) (cm^{-1})	δ(NCO) (cm^{-1})
KOCN	(calc.)	r.t.	2165^{a}	1301.5^{b} 1207.3^{d}	636.9^{c} 628.0^{e}
KOCN	KBr	295	2169.2	1299.2 1205.7	637.6 628
	KBr	80	2171.2	1301.1 1205.7	638.5 628
Pt[bpy(NCO)$_2$]	KBr	295	2257sh 2230	1345	(604) 580
	KBr	82		1345	610 579
	Kel-F mull	295	2246(sh) 2232	n.o.	n.o.
	mull	r.t.	2225 2215	1340	576
	NMP solution	295	2251(sh) 2230	n.o.	n.o.
Pt[L(2)(NCO)$_2$]	KBr	295	2270(sh) 2246	1347	580
	KBr	82	2247	1348 1337	577 601
Pt[L(3)(NCO)$_2$]	KBr	295	2259^{f}	1348	584
	Kbr	82	2273br	1349	
Pt[L(4)(NCO)$_2$]	KBr	295	2254br	1349	587
Pt(NCO)$_4^{2-}$	Nujolmull	r.t.	2299–2190vbr	1319m	613, 604m, 594
	CH$_3$NO$_2$ solution	r.t.	2203vvs	n.o.	614, 595s

L(2) = 4,4′-(CH$_3$)$_2$ bpy; L(3) = 5,5′-(CH$_3$)$_2$ bpy; L(4) = 4,4′-(Ph)$_2$ bpy. $^{a}\nu_3$. $^{b}2\nu_2$. $^{c}\nu_{2b}$. $^{d}\nu_1$. $^{e}\nu_{2a}$. ^{b} and ^{d} are split by Fermi resonance with $2\delta_{NCO}$ (1271.24 cm^{-1}). ^{f}v. broad.

solvent was chosen since it was employed as the solvent of choice in the NMR experiments (*vide infra*). The CN stretch absorption in the KBr matrix consists of an asymmetric band which represents the unresolved envelope of the two infrared active modes expected for a *cis*-(NCO)$_2$ configuration. The approximqate $\nu_{1/2}$ value is 45 cm^{-1}. The broad absorbance profile noted for the CN stretching mode in N-bonded cyanates has been commented on by a number of authors [35, 40, 41], and appears to be a general property of this class of pseudohalide metal complexes, rather than a limitation of the spectroscopic treatment of the samples. In contrast to the IR spectra of Pt(bpy)(CN)$_2$, as well as of Pt(bpy)(SCN)$_2$ dispersed in a mull (Kel-F), for which the two expected active CN stretching modes are readily resolved, no such resolution was observed in the case of Pt(bpy)(NCO)$_2$ (Fig. 2) for which the band profiles in Kel-F and KBr are very similar. In NMP, the two bands are slightly better resolved, but the $\nu_{1/2}$ value has increased to approximately 72 cm^{-1}, in agreement with the nitromethane solution data of Norbury and Sinha [6]. It is worth noting, however, that the CN stretch observed by the latter in their mull spectra (using a dispersive spectrometer) is at significantly lower frequency than those reported in the present work. The close resemblance between the KBr and solution absorption profiles (Fig. 2) provides some support for the assumption that the chemical species probed by the IR measurements, and those present in the NMR experiments are identical.

The frequency of the more intense CN stretching mode shows the usual blue shift of ~5 cm^{-1} when the KBr matrix is cooled to 80 K, without, however, effecting resolution of the underlying two bands. The shoulder at ~2265 cm^{-1} cannot be located with any meaningful precision from the present data. The broad ν(CN) band profile (Fig. 2), and the concomitant lack of resolution of the two CN stretching modes, which is not significantly temperature dependent, may be accounted for by postulating a coupling between symmetry-allowed low frequency librational ligand modes, and the normal modes corresponding to the CN stretch of the pseudohalide. The combination bands resulting from these inter-

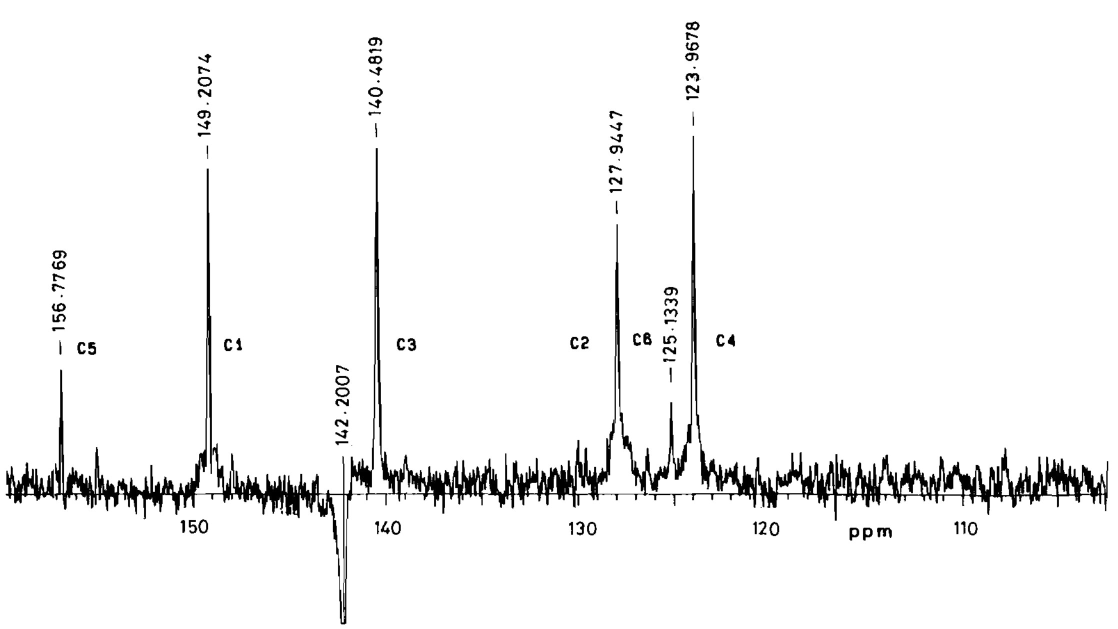

Fig. 3. ^{13}C NMR spectrum of $Pt[(2,2'\text{-bpy})(NCO)_2]$ in *N*-methyl pyrrolidone solution at room temperature. The resonance assignments correspond to the numbering scheme in Fig. 1. The resonance at 125.1 ppm is assigned to the C atom of the pseudohalide ligand, and its position is taken as diagnostic of N-bonding in the complex present in solution. (The spectral feature at 142 ppm is an instrument artifact and should be ignored.)

TABLE 7. ^{13}C NMR data (ppm) at 295 K

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	NC X	Notes
2.2'-bipyridyl	156.4	121.4	137.2	124.0	149.4	–	a
$(bpy)PtCl_2$	156.8	124.2	140.5	127.7	148.3	–	b
$(bpy)Pt(SCN)_2$	156.4	124.8	141.8	128.5	148.1	114.6	c
$(bpy)Pt(NCO)_2$	156.8	124.0	140.5	128.0	149.2	125.1	c
$(py)_2Pt(SCN)_2$	153.2	127.3	139.0	127.3	153.2	114.1	c, d
$(bpy)Ru(NCS)_2$	158.3	123.4	136.5	126.9	152.2	133.4	e
	157.0	123.3	135.7	126.2	151.5		

[a]In $CDCl_3$, ref. 42. [b]In d_6 dimethyl sulfoxide. [c]In *N*-methyl pyrrolidone with dmso internal standard. [d]*trans* isomer. [e]*cis* isomer, dmso and CH_3CN solvates, ref. 13.

actions are not resolvable, even at the low temperature limit (*c.* 6 K) of the FT-IR spectrometer. Some support for this interpretation may be drawn from the observation that in certain pseudohalide spin-crossover complexes, which are constituted from similar bidentate ligands (e.g. bpy, phen and their ring-substituted homologues), in cases where the high-spin doublet remains unresolved due to a broad absorbance envelope even at low temperatures, the low-spin doublet, which is blue-shifted by *c.* 50 cm^{-1}, can be readily resolved in the IR spectra.

^{13}C *NMR data*

The NMR data acquired in the present study addresses bonding aspects of two moieties of the title compound: the bpy ligand and the NCO ligand. A representative spectrum is shown in Fig. 3, and the relevant data are summarized in Table 7. With respect to the bonding of the bidantate ligand, there is nothing particularly remarkable in the ^{13}C data pertaining to the bipyridyl fragment [42]. The observed number of resonances assigned to these carbon atoms do, however, confirm the two-fold symmetry of the bidentate ligand, even in solution. Coordination to platinum results in essentially no shift in the C(2) and C(6) resonances, and shifts of 2.9, 3.7 and 4.1 ppm, respectively in the C(3), C(4) and C(5) resonances. The ^{13}C chemical shift of the pseudohalide ligand, placed at 125.1 ppm, is diagnostic of an N-bonded NCO ligand, using the systematics reported by Wehrli and Wirthlin [43]. These authors have shown that — although there is a small overlap between the two ranges — O-bonded NCO groups show a resonance lying between 104 and 119 ppm, while N-bonded groups evidence this signal in the range 114 to 132 ppm. The observed signal at 125.1 ppm, assigned to the pseudohalide carbon atom, is thus taken as indicative on an N-bonded ligand in this complex in solution. A similar diagnostic inference for the cyanate, thiocyanate and selenocyanate moieties has been discussed by Burmeister *et al.* [44, 45] and others [46] although there is again a region of chemical shifts where this measure must be exercised with caution. An application of these systematics to copper thiocyanate complexes has been reported by Zumbulyadis and Gysling [47]. Despite this possible uncertainty, however, the present evidence is clearly consistent with an N-bonded cyanate group, and lends support for the refinement referred to above in the discussion of the X-ray data. Chew *et al.* [48] have similarly made use of ^{14}N chemical shift data to show that in ligating to a variety of metals, the cyanate ligand is preferentially coordinated through the N atom, and the Pt(II) complex of the present study appears to be no exception to this rule. In fact, to the best of our knowledge, to data, no O-bonded heavy metal non-bridging cyanate complexes [49] have been reported in the crystallographic literature.

Further studies of Pt(II) pseudohalide complexes, especially their tendency to form metal–metal bonded polymers, is currently underway in these laboratories.

Supplementary material

Table SI, listing observed and calculated structure factors, is available from the authors on request.

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