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Ligand Configuration on Weakly Paramagnetic (β-Imino carbonyl enolato)nickel Complexes: A Combined Solid-State ^{13}C NMR and Infrared Study

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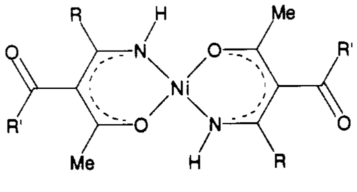
The two forms of the $[Ni((MeCO)_2CC(COPh)NH)_2]$ complex resulting from the reaction of bis(acetylacetonato)nickel(II) with benzoyl cyanide have been studied by ^{13}C CP/MAS NMR and FT-IR techniques. Despite their paramagnetism (μ = 0.61 (form I), 0.57 (form II) μ_B), the ^{13}C signals in the solid state are narrow and well resolved, so that specific isotopic enrichment allows a safe signal attribution. In both cases the data indicate that the trifunctional (N,O,O) β-imino carbonyl enolato ligand is bonded to the nickel center via the nitrogen and oxygen atoms. The same behavior and type of ligand coordination is observed in the two forms of the related cyanogen derivative $[Ni((MeCO)_2CC(CN)NH)_2]$ (μ = 0.68 and 0.50 μ_B). A correlation is found between the carbonyl chemical shift of the uncoordinated acetyl group and its torsion angle relative to the {NiNONO} plane, which indicates that, for both complexes, the two isolable forms are ligand conformation isomers.

β-Imino carbonyl enolato complexes are characterized by the presence in the coordination sphere of monoanionic ligands bearing an N,O,O atom donor set capable, in principle, of various bonding modes to the metal center. We are particularly interested on this class of compounds as they result in being important intermediates in the metal-catalyzed synthesis of a large variety of β-enamino diones, starting from β-dicarbonyls and nitriles.[1-9] Clearly full characterization of these complexes, with special attention to their ligand configuration, may be fundamental in defining their role in the catalytic process and in finding better synthetic conditions. To this purpose, the potentiality of solid-state ^{13}C CP (cross polarization) MAS (magic angle spinning) NMR has been checked, when applied also to weakly paramagnetic complexes, supporting the results with an accurate IR study. The prototype compounds are the square planar $[Ni((MeCO)(R'CO)CC(R)NH)_2]$ complexes



which can be obtained by reaction of nickel β-carbonyl enolates with benzoyl cyanide or cyanogen. The acetylacetonato derivatives are isolable in the solid state in two stable forms, whereas only one is observed for the benzoylacetonato complex [**1**, R = COPh; R' = Me (**1a**, **1b**); **2**, R = COPh, R' = Ph;[10] **3**, R = CN, R' = Me (**3a**, **3b**)].[11-13]

They all possess a low paramagnetism at room temperature (μ = 0.50–1.23 μ_B); the structure sketched above (N,O coordination) has been determined by X-ray analysis for **1b** and **3b**,[10,13] i.e. for one of the two forms, which were indicated in the literature as form II for R = COPh and form β for R = CN, while no definite evidence on the type of ligand coordination is available for the other investigated compounds.

Experimental Section

Synthesis of the Complexes. The $[Ni((MeCO)(R'CO)CC(COPh)NH)_2]$ complexes were prepared, as previously reported,[10] by reaction of nickel acetate with the appropriate β-benzoyl β-enamino dione ligand in ethanol. With this procedure $[Ni((MeCO)_2CC(COPh)NH)_2]$ was obtained in form I (**1a**), which was transformed into form II (**1b**) by recrystallization from commercial dichloromethane. The ligands were obtained by metal-catalyzed reaction of acetylacetone (C. Erba) (or benzoylacetone (EGA)) with benzoyl cyanide (Fluka);[4] ^{13}C-labeled ligands used PhCOCN enriched (99%) in the CO or CN carbon atom. Labeled benzoyl cyanide was, in turn, synthesized by reaction of equimolar $Ph^{13}COCl$ (Aldrich) with KCN or of PhCOCl (Aldrich) with $K^{13}CN$ (Cambridge Isotope Laboratories) in benzene, in the presence of 18-crown-6 (Aldrich). The $[Ni((MeCO)_2CC(CN)NH)_2]$ complex (α (**3a**) and β (**3b**) forms) was prepared by reaction of bis(acetylacetonato)nickel(II) with cyanogen (Fluka) or labeled cyanogen ($^{13}C_2N_2$) as previously reported.[13]

NMR Analysis. ^{13}C CP/MAS NMR measurements were performed on a Bruker AM 250 spectrometer operating at 250.19 MHz for ^{1}H and at 62.89 MHz for ^{13}C. The setting of the magic angle was monitored by recording the ^{79}Br NMR spectrum of KBr. Cross polarization (CP) was obtained according to conventional procedure. Samples (ca. 250 mg) were introduced in a double-bearing zirconia rotor (7-mm/o.d.) and spun at the magic angle with a frequency of 4.2 KHz. ^{13}C CP/MAS

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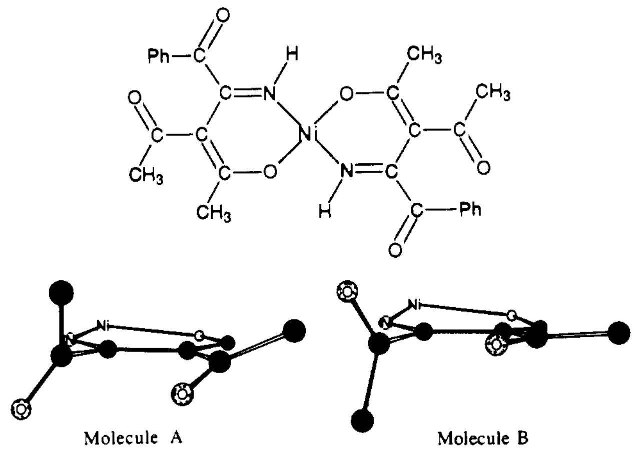


Figure 1. Schematic structure of one form of [Ni((MeCO)$_2$CC(COPh)NH)$_2$] (**1b**) and a partial view from the same side of the two centrosymmetric molecules A and B contained in the unit cell.

NMR spectra were recorded with the pulse sequence reported by Dixon et al.[14] for the suppression of the spinning sidebands. A 2-ms contact time, with a repetition delay of 3 s between the scans over 2000 transients, was also used. The chemical shifts were referenced to external liquid tetramethylsilane (TMS), using as secondary reference the methylene carbon signal of adamantane at 38.3 ppm downfield from TMS.

IR Measurements. The infrared spectra in the range 4000–80 cm^{-1} were measured at 1-cm^{-1} resolution with the Bruker IFS 66 FT IR spectrometer (KBr and Mylar 6-μm beam splitters). Samples studied were in KBr or crystalline polyethylene pellets.

Results and Discussion

All complexes exhibit, despite their paramagnetism, well-resolved narrow ^{13}C signals in the solid state, and specific labeling leaves no doubt about the signal attributions. The results can be discussed in the light of the published structures to find a correlation between ligand configuration and observed chemical shift of the carbon atom in the various functional groups.

[Ni((MeCO)$_2$CC(COPh)NH)$_2$] can be isolated in two forms (**1a**,**1b**), and an X-ray analysis has shown that the unit cell of **1b** contains two independent chemically identical molecules, whose structure is sketched in Figure 1.[10]

The two molecules exhibit, within experimental errors, identical bond distances and angles, and both do not evidentiate any intermolecular interaction, the only differences lying in the torsion angles of the benzoyl and acetyl groups. The dihedral angles between the {NiNONO} and {CCOPh} planes are 72.0° for molecule A and 76.8° for molecule B, with the benzoyl oxygen atom facing the imino hydrogen in both cases. The variation of the corresponding dihedral angle for the acetyl group is somewhat greater, and it changes from 29.1° (molecule A) to 8.8° (molecule B). This small structural difference has important effects on the solid-state ^{13}C chemical shifts of the two molecules; in fact compound **1b** exhibits two distinct sets of resonances, which can be, at least in part, individually attributed (Table I and Figure 2). Four resonances in the range δ = 29.2–31.7 ppm are indicative of four magnetically nonequivalent methyl carbon nuclei in the two molecules. Six carbonyl signals are also observed in the region 184.6–199.9 ppm, and specific ^{13}C enrichment of the benzoyl carbon produces a growth of the signals at 189.4 and 191.5 ppm. These values are slightly low for a carbonyl bonded to an aryl group[15] and seem to indicate a moderate reduction of the C=O bond order. The remaining four resonances can be divided into two couples at lower (184.6 and 186.8 ppm) and higher (193.6 and 199.9 ppm) chemical shifts. Values like these are typical of the acetyl groups of M–acac complexes in solution (δ = 186–195 ppm)[16] and compare well with those found, in the solid state, for the anhydrous and hydrated forms of bis(acetylacetonato)zinc(II).[17] Values in the first range are easily associated with carbonyl carbon nuclei in the chelate ring; meanwhile values falling in the second range are attributable to uncoordinated CO's. With reference to Figure 1, this does not mean that we are dealing with pure single and double carbon–oxygen bonds, respectively, but it simply indicates that delocalization of π electrons of the ring involves in a reduced manner the external acetyl group, which maintains a more pronounced double-bond character. For details of this last aspect, a particular comment is required by the large difference of the pertinent chemical shift in the two molecules (193.6 vs 199.9 ppm); this behavior can be discussed on considering the possible canonical structures I and II. When bond delocalization minimizes differences in bond distances, a useful criterion for assessing the relative weight of the two structures may be the torsion angle of the acetyl group with respect to the coordination plane.[18,19] High values for this angle indicate free rotation along the C–C bond and a great prevalence of structure I, low values being indicative of an increasing importance of II. As a consequence, the observed differences of carbonyl chemical shifts can be explained in the light of different contributions of the two limit forms; the higher δ value (almost pure CO double bond) can be attributed to molecule A, which, having a torsion angle of 29.1°, is closer to structure I than molecule B (torsion angle 8.8°). With similar reasoning, but in a more speculative way, could be discussed the individual attributions for the other couples of signals. It is remarkable, anyway, that for every type of carbon nucleus two distinct signals are obtained at the appropriate chemical shift

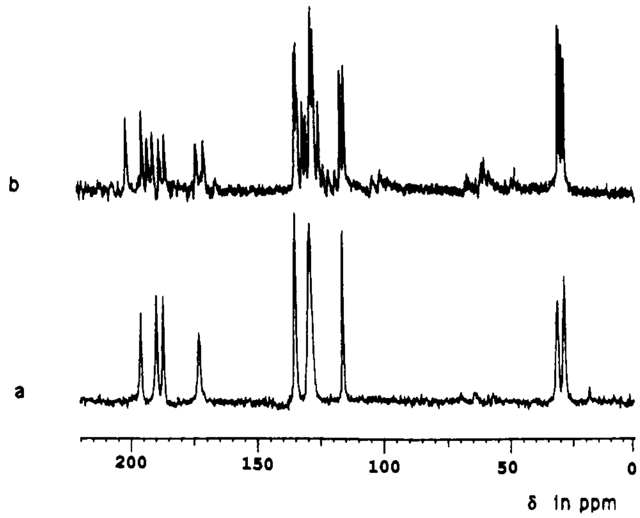
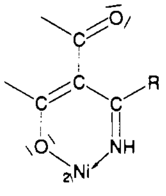


Figure 2. ^{13}C CP/MAS NMR spectrum of the two forms of [Ni((MeCO)$_2$CC(COPh)NH)$_2$] (a = **1a**, b = **1b**).



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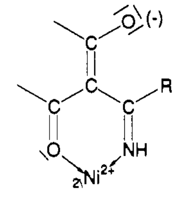

II

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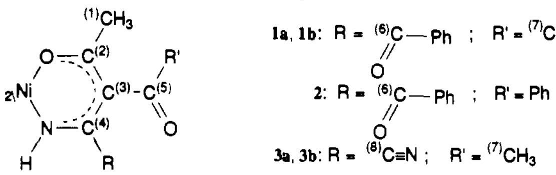
Table I. ^{13}C NMR Data for the [Ni((MeCO)(R'CO)CC(R)NH)$_2$] Complexes

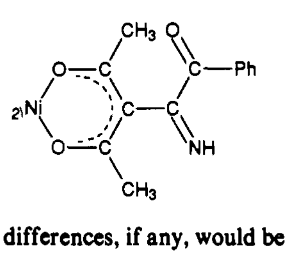


C atom	solid state					solution^a	
	1a	**1b**	**2**	**3a**	**3b**	**1a** or **1b**	**2**
1	28.6^b	29.2^b	24.7	28.8	27.3		
1		30.0^b					
7	31.4^b	31.0^b		31.4	32.3	31.1	
7		31.7^b					
8				115.0^c	112.3^c		
3	116.0	116.2	113.7	115.7	118.5	116.5	114.7
3		117.7					
4	173.0	169.4	168.3	141.6	140.9	173.0	172.6
4		172.3					
2	186.8	184.6	181.2	189.7	186.6	187.4	186.0
2		186.8					
6	189.5	189.4	190.7			193.5^d	
6		191.5					
5	195.7	193.6	195.6	196.8	202.7	195.6	194.7
5		199.9					
Ph	129.3–135.2	126.2–135.7	128.4–141.1			128.2–135.0	128.3–140.8

^{a} (CD$_3$)$_2$SO solution, at 25 °C, δ in ppm from TMS. Solution ^{13}C spectrum of **3a** or **3b** undetectable. ^{b} Tentative attribution based on the correlation found in solution between methyl and carbonyl resonances. ^{c} The signal due to cyano carbons appears as two lines with a 2:1 intensity ratio and spacing (S) of 4.2 ppm. The reported chemical shifts were calculated by subtracting $^1/_3S$ from the chemical shift of the line with the higher intensity. ^{d} Detectable only in the enriched complex **1**-^{13}CO.

values, with an excellent correspondence between structural and spectroscopic parameters.

As concerns the other form of [Ni((MeCO)$_2$CC(COPh)NH)$_2$] (**1a**), it was impossible to obtain crystals adequate for an X-ray analysis, so that, despite a careful chemicophysical investigation, strong uncertainties remained on its structure. The obtained solid-state ^{13}C NMR spectrum exhibits a number of signals half with respect to **1b**, so that only one type of molecule is present in this case, but the general resonance pattern is strictly similar (Figure 2). Particularly interesting to our purpose appear the chemical shift values of the carbonyl carbon nuclei. ^{13}C labeling allows one to attribute the signal at 189.5 ppm to the benzoyl carbon and the remaining two to the acetyl carbon nuclei. The absolute values of their chemical shifts (δ = 186.8 and 195.7 ppm) and the large difference in between (Δδ = 8.9 ppm) indicate a chemical environment markedly different for the two nuclei and seem to rule out the alternative possibility of an O,O coordination to the metal center, according to a structure of the following type:



In fact, very small differences, if any, would be expected, in this case, for the resonances of the two coordinated carbonyl groups; also the almost invariancy of the imino carbon resonance of **1a** with respect to form **1b** [173.0 vs 172.3 (or 169.4) ppm] is consistent with the hypothesis that **1a** has the same N,O ligand coordination of **1b**.

Infrared data (Table II and Figure 3) further confirm this hypothesis; in fact, as the whole, the spectra of the two forms are very similar, taking into account an almost double number of peaks for **1b**; in addition, ^{13}C labeling produces an identical effect on the two spectra. In particular, the peaks at 1670 (**1a**) and 1676 and 1665 (**1b**) cm^{-1} are unequivocally attributed to a pure (Ph)C=O stretching, as they fall in the expected frequency range[20] and undergo a shift of 36–37 cm^{-1} on specific CO labeling. The absorptions around 1630 cm^{-1} [1634 (**1a**), 1628 and 1623 (**1b**) cm^{-1}], which are *totally unaffected* by ^{13}C labeling both at the (Ph)C=O and CN(H) groups, are associated with the CO stretching of uncoordinated acetyl groups. They cannot be attributed to a coordinated carbonyl in a chelate ring, as the pertinent wavenumber values should be below 1600 cm^{-1}.[21] Moreover, the residual possibility (for **1a**) of attributing the absorption to the C=N stretching of an external (PhCO)C=NH group in an O,O ligand coordination mode is ruled out by the lack of any isotopic effect on this band. The wavenumber values of these acetyl absorptions (one for **1a** and two for **1b**) are ca. 80 cm^{-1} lower than those of saturated alkyl ketones,[20] so indicating reduction of the double-bond character of the carbonyl group, as a consequence of some donation of π electron density to the chelate ring. This mesomeric effect, which is different for the two independent molecules of **1b**, seems to involve scarcely the benzoyl CO, in accord with the previous considerations on the relation between bond order and torsion angles of the substituents at the ring. This result thus confirms that also **1a** *must* have an uncoordinated acetyl group and, as a consequence, an N,O ligand coordination. The individual attributions of the various absorptions in the chelate ring are complicated by combination modes; only the peak at 1559 cm^{-1} (**1a**) [1565 cm^{-1} (**1b**)] is markedly affected by ^{13}CN(H) labeling [−27 (**1a**) and −29 (**1b**) cm^{-1}], thus being attributable to a prevalent C⋯N stretching, with a possible C⋯C contribution.

Absorptions in the metal–ligand vibration region (600–80 cm^{-1}) appear often as composite bands for **1b**, as it may have been expected from the presence of two distinct molecules. These absorptions are generally stronger than in **1a**, suggesting a more symmetrical arrangement for the latter. These bands do not give definite information with respect to ligand coordination in **1a**, although the presence of three bands at 427, 401, and 340 cm^{-1} seems indicative of an N,O bonding set.[21]

On the whole, these NMR and IR data on the solid-state structures of the two isolable forms of [Ni((MeCO)$_2$CC(COPh)-

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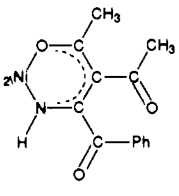
Table II. IR Spectral Data for the [Ni((MeCO)$_2$CC(COPh)NH)$_2$] Complexes[a]



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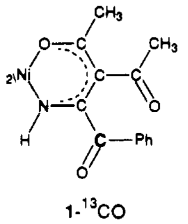
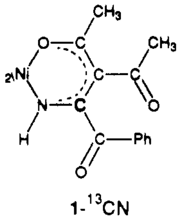


1-^{13}CO



1-^{13}CN

	1a	**1a**-^{13}CO	**1a**-^{13}CN	**1b**	**1b**-^{13}CO	**1b**-^{13}CN
ν(N–H)				3301	3301	3301
ν(N–H)				3297	3297	3297
ν(N–H)	3276	3275	3274	3275	3267	3267
ν((Ph)C═O)	*1670*	*1634*	1670	*1676*	*1639*	1675
ν((Ph)C═O)				*1665*	*1628*	1664
ν((Me)C═O)	1634	1634	1633	1628	1628	1627
ν((Me)C═O)				1623	1623	1621
ν(C⋯O)	1596	1595	1596	1598	1597	1598
ν(C⋯O) + ν(C⋯C)	1579	1577	1579	1579	1578	1579
ν(C⋯N) + ν(C⋯C)	*1559*	1559	*1532*	*1565*	1564	*1536*
ν(CC(arom))	1492	1491	1492	1492	1492	1492
				1460	1460	1458
	1451	1450	1451	1451	1450	1450
				1443	1443	1441
	1407	1407	1407	*1422*	1421	*1415*
	1390	1390	1388	1398	1398	1397
	1364	1364	1364	1365	1365	1362
	1354	1354	1354	1357	1357	1356
				1344	1344	1342
	1307	1307	1307	1311	1311	1311
				1303	1303	1303
ν(C–COPh)	*1263–1252*	*1249–1240*	1261–1249	*1245*	*1232*	1243
	1176	1175	*1171*	1177	1177	1176
				1166	1165	*1159*
				1156	1156	1155
				1069	1069	1069
	1065	1064	1064	1065	1065	1065
	1040	1037	1038	1040	1038	1039
	1025	1025	1025	1025	1024	1025
	1000	1000	1000	1002	1001	1002
	976	*970*	975	973	971	973
	962	959	962	961	958	960
				938	938	938
				927	926	927
	843	*839*	838	848	848	848
	818	*813*	818	*825*	*821*	824
	793	*790*	790	*799*	*793*	795
				769	769	768
	756	754	*749*	*753*	752	*749*
	732	729	*726*	*745*	744	*737*
	715	714	715	719	718	717
	697	697	697	698	697	698
	688	688	688	689	689	689
	664	*660*	664	*662*	*658*	662
	649	647	647	*657*	*651*	656
	635	633	635	636	635	636
	617	617	617	616	615	616
				613	611	611
	594	591	*590*	*594*	591	*590*
	537	537	537	535	535	534
	486	486	486	478	478	477
	458	455	457	*456*	*452*	456
				444	444	444
	427	425	427	425	424	425
	401	401	401	402	402	402
	340	339	340	349	347	348
	288	287	288	289	287	288
	270	270	270			
	242	242	242	240	240	240
	175	175	175	211	211	211
	160	160	160	181	180	181
	114	114	114	116	116	116
				98	97	97

[a] In KBr + crystalline polyethylene pellets; significant isotopic shifts are in italics.

NH)$_2$] are fully consistent with the N,O coordination mode proved by X-ray analysis for **1b** and definitely support the same set of ligating atoms for **1a**. Thus, the source of their distinct chemicophysical characteristics (e.g. NMR and IR spectra,

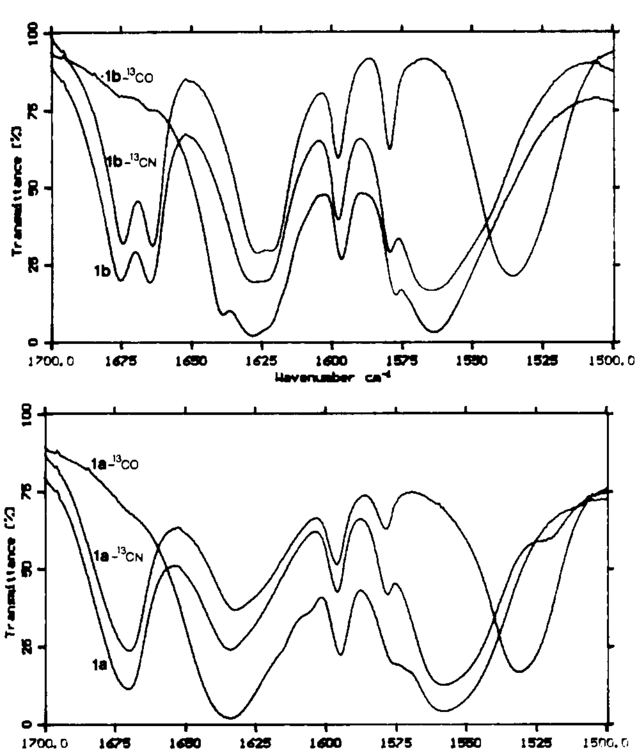


Figure 3. FT IR spectra of the two forms of $[Ni((MeCO)_2CC(COPh)NH)_2]$ (**1a**,**b**) and of their ^{13}C-enriched derivatives (key figures in Table II) in the range 1700–1500 cm^{-1}.

thermal behavior (TG-DSC), X-ray powder diffraction pattern)[10] may lie in small differences of ligand conformation, as the consequence of different torsion angles of the substituents at the chelate ring. In this view, it is perhaps not coincidental that the carbonyl resonance of the uncoordinated acetyl group of **1a** falls at 195.7 ppm, a value which is between those found in the two molecules of **1b** (193.6 and 199.9 ppm). ^{13}C CP/MAS NMR spectra up to 110 °C of **1a** show only a weakening of the phenyl signals, so indicating that the rotation of the acetyl and benzoyl groups is rather hindered in the solid state.

The solution structure of the two forms of **1** was also studied by NMR spectroscopy (Table I). The ^1H and ^{13}C spectra of a $(CD_3)_2SO$ solution of **1a** and **1b** are identical, so indicating easy conversion to a unique stable molecular structure. The ^1H spectrum[10] shows two signals due to the methyl groups at 2.25 and 2.42 ppm, while aromatic protons resonate in the range 7.4–7.7 ppm and imino proton at 7.30 ppm. By contrast, in the ^{13}C NMR spectrum there is only one resonance at 31.1 ppm for methyl carbons and two signals at 195.6 and 187.4 ppm, corresponding respectively to the uncoordinated and to the coordinated carbonyl carbon atoms. A 2D heteronuclear (C, H) shift correlation experiment (2D hetero-COSY)[22] through J^2 (C, H) coupling constant shows that the methyl resonances at 2.25 and 2.42 ppm in the ^1H NMR spectrum are correlated to the signals at 195.6 and 187.4 ppm in the ^{13}C NMR spectrum attributed to the uncoordinated and coordinated acyl groups, respectively. In addition, a residual correlation observed in this 2D hetero-COSY experiment assigns the resonance at 31.1 ppm in the ^{13}C spectrum to the methyl carbon bonded to the external carbonyl group. Surprisingly, one can not observe the ^{13}C signals corresponding to the methyl (^1H resonance at 2.42 ppm) and carbonyl groups of the ring substituents in β positions to the nickel atom. Most probably the interaction between the substituents in this particular position and the paramagnetic nickel center makes the signals too broad to be detectable. As a matter of fact, the comparison between the ^{13}C spectrum of **1a** and that of the corresponding ^{13}C-enriched benzoyl CO sample shows the presence of an additional resonance at 193.5 ppm attributable to the enriched carbonyl group. As a final comment on this point, it should be underlined the similarity, where comparable, of the spectra in the solid state and in solution, which strongly suggests the same molecular structure in the two phases.

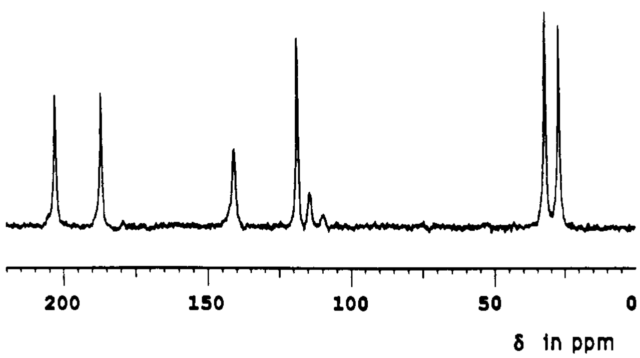


Figure 4. ^{13}C CP/MAS NMR spectrum of one form of $[Ni((MeCO)_2CC(CN)NH)_2]$ (**3b**).

Passing to consideration of the ligand coordination in the benzoylacetonato $[Ni((MeCO)(PhCO)CC(COPh)NH)_2]$ (**2**) complex, its solid-state ^{13}C NMR spectrum unambiguously indicates metal coordination of the acetyl group. In fact, a resonance is found at 181.2 ppm, which is attributed to a carbonyl carbon nucleus with a largely reduced double-bond character; moreover, the concomitant low value of the observed methyl carbon chemical shift ($\delta = 24.7$ ppm) let it to individuate as an acetyl CO on the basis of the known parallelism of deshielding effects on the two adjacent carbon nuclei. The imino carbon resonance falls at $\delta = 168.3$ ppm, a value very close to that found in the corresponding acetylacetonato derivative, so suggesting the same nitrogen–metal coordination. The possibility of a (Ph)-CO coordination seems excluded by the fairly high chemical shifts at 190.7 and 195.6 ppm, which are attributable, respectively, to the carbonyl resonances of the benzoyl groups in β and γ positions in the ring.

This conclusion is supported by the NMR data in $(CD_3)_2SO$ solution; the ^1H spectrum shows the methyl and phenyl resonances at the expected chemical shifts,[10] whereas in the ^{13}C spectrum again are not observed the signals due to the methyl and to one carbonyl group. By comparison with the solid-state spectrum and by analogy with the observed behavior of the acetylacetonato derivative, one can safely attribute the resonances at 172.6 and 186.0 ppm to metal-coordinated imino and carbonyl groups. Furthermore, the methyl group, whose ^{13}C resonance is missed, should be in a β position in the chelate ring with respect to the nickel center, so that the benzoyl groups appear not involved in coordination.

The validity of solid-state NMR measurements in determining ligand coordination mode finds confirmation in the study of the related $[Ni((MeCO)_2CC(CN)NH)_2]$ (**3**) complex (Table I). Also this complex can be isolated in two forms (**3a**,**b**); the structure of **3b** has been determined by X-ray analysis, and a careful IR investigation has suggested that **3a** has the same N,O ligand coordination found for **3b**.[13] The ^{13}C NMR solid-state spectra are fully consistent with the previous results: **3b** (Figure 4) exhibits two CO resonances at 186.6 and 202.7 ppm, which are easily attributed to coordinated and uncoordinated carbonyl carbon nuclei; the value of this last one is particularly high and, according to the previous considerations, can be explained on the basis of an almost pure carbon–oxygen double bond. The large dihedral angle formed by the acetyl substituent with the {NiNONO} coordination plane (39.5°)[13] would, in fact, indicate a scarce π-electron donation from the substituent to the chelate ring.

The imino and cyano carbon nuclei show complex patterns

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[22] Bax, A.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 501.

centered at 141 and 112 ppm. As reported in the literature,[23] the presence of quadrupolar nuclei, such as ^{14}N, may introduce additional complications in the ^{13}C CP/MAS NMR spectra through the residual ^{13}C, ^{14}N dipolar coupling which is not averaged to zero by MAS. In the case of a ^{13}C coupled to a single ^{14}N, the spectrum consists of a pair of lines with intensities in the ratio 2:1, whose relative position depends on the value and sign of the splitting expected on the basis of geometric and energetic factors related to the C–N bond. Since the splittings induced by imino nitrogens are predicted to be small, the signals due to the imino carbon in the chelate ring appear in the ^{13}C CP/MAS NMR spectra as a broad singlet. By contrast, in the case of the nitrile, the resonance corresponding to the cyano carbon appears as two broad lines, with the expected 2:1 intensity ratio and a spacing of 260 Hz.

Again, as in the case of the benzoyl cyanide derivatives, the other form (**3a**) shows a similar pattern (Figure 5), with, in particular, two well-separated carbonyl resonances at 189.7 and 196.8 ppm, which strongly indicate that only one acetyl group is coordinated to the nickel center. Its spectrum in the region 111–142 ppm is complicated by an overlapping of signals; however, the use of labeled $[Ni((MeCO)_2C^{13}C(^{13}CN)NH)_2]$ allows one to identify from the difference spectrum the resonances attributable to the cyano, imino, and intercarbonylic carbon nuclei. It results that the imino signal of **3a** falls at a chemical shift value very close to that of **3b** (141.6 vs 140.9 ppm), so confirming the same nitrogen coordination to the metal proposed on the basis of an IR study.[13]

Thus, $[Ni(acac)_2]$ reacts with PhCOCN or C_2N_2 in a very similar manner to give two isolable forms, which appear as ligand conformation isomers. It may be assumed that the conformers which precipitate first (**1a** and **3a**) have a geometry where planarity and bond delocalization involves to some extent also the acetyl group external to the chelate ring. These forms are slightly unstable and convert to **1b** and **3b** in a more stable crystal packing, which may require a variation of the torsion angle of the acetyl with respect to the coordination plane. In fact, the value of the ^{13}C CO resonance should reflect its degree of double-bond character, so that it may be possible to correlate, for a series of strictly similar compounds, the carbonyl chemical shift of the uncoordinated acetyl group with the values of the corresponding dihedral angle between MeCO and {NiNONO} planes for **1b** [29.1° (molecule A) and 8.8° (molecule B)][10] and for **3b** (39.5°).[13] From the good linear relation obtained (intercept 191 ppm and slope 0.3 ppm/deg) it is possible to extrapolate the approximate value of the same angle for **1a** (16°) and **3a** (20°). It is remarkable in this context that a similar value was proposed for **3a** on the basis of the close analogy of its X-ray powder diffraction spectrum with that of the related copper complex.[13]

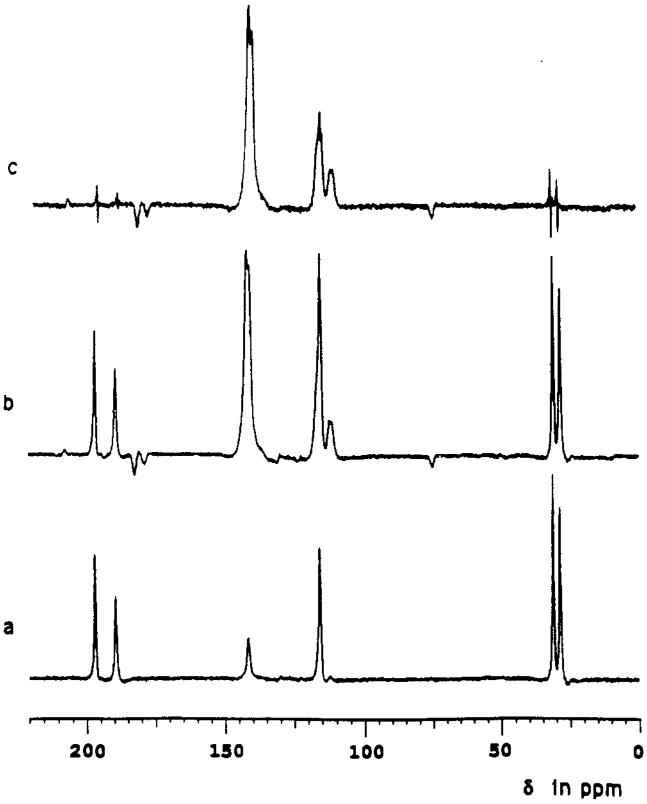

Figure 5. ^{13}C CP/MAS NMR spectra of one form of $[Ni((MeCO)_2CC(CN)NH)_2]$ (**3a**) (a) and of its $^{13}C_2N_2$-enriched derivative (b), with the difference spectrum at the top (c).

This study emphasizes the use of solid-state NMR spectroscopy in the full characterization of complexes, even when they are weakly paramagnetic, overcoming the limitation of solution studies. This technique allows one not only to define the type of ligand coordination but also to solve subtle problems of ligand conformation, when direct X-ray single-crystal determination is not accessible.

Acknowledgment. We thank Mr. A. Ravazzolo for skilled technical assistance.

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(23) Olivieri, A. C.; Frydman, L.; Grasselli, M.; Diaz, L. E. *Magn. Reson. Chem.* **1988**, *26*, 281.