# N,O *versus* O,O′ Co-ordination in β-Iminodiketonato Complexes: a Reinvestigation†

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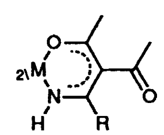
The solid-state structures of the iminodiketonato complexes obtained in the reaction of cyanogen with [M(acac)$_2$] (M = Ni or Cu, acac = acetylacetonate) and [Cu(bzacen)] (bzacen = Schiff base anion formed between ethane-1,2-diamine and benzoylacetone) have been reinvestigated. The X-ray data have been recollected, under improved conditions, for one form of [Ni(acac·C$_2$N$_2$)$_2$] (labelled β) and the structure determined according to an N,O co-ordination mode. This model gives a better crystallographic *R* factor compared with the previous one based on an O,O′ atom ligating set (0.029 *vs.* 0.047) and, in addition, clearly indicates the presence of the imino hydrogen. The structures of the analogous copper derivative and of [Cu(bzacen·2C$_2$N$_2$)] have been recalculated from the reported data and, also in these cases, the hypothesis of N,O co-ordination improves the refinement of the data (*R* = 0.055 *vs.* 0.062 and 0.060 *vs.* 0.081, respectively). An accurate Fourier-transform IR study, including $^{13}$C labelling, of the two forms (α and β) in which [Ni(acac·C$_2$N$_2$)$_2$] can be isolated indicates that this co-ordination mode is also adopted by the α form, which is thus a ligand conformation isomer of the β form.

We have discovered an unprecedented behaviour of cyanogen in its co-ordination chemistry,[1] *i.e.* its susceptibility to undergo nucleophilic attack by the intercarbonylic carbon atom of β-carbonylenolato rings. The consequent facile formation of a carbon–carbon bond coupled with favourable kinetic and thermodynamic parameters made it possible to develop a general metal-catalysed synthesis of β-enaminodiones from β-dicarbonyls and nitriles, under very mild conditions.[2–10]

The nature of the addition products stemming from the reaction of metal-β-carbonylenolato rings with cyanogen has been proposed in the various cases either on the basis of X-ray single-crystal studies or of a combination of more or less tangential chemical evidence. Most attention was centred on the acetylacetonato derivative [Ni(acac·C$_2$N$_2$)$_2$], which can be isolated in two forms (α and β) differing in their solid-state IR spectra, X-ray powder diffraction, and thermogravimetric and differential thermoanalytical profiles: in all cases the experimental data were interpreted in terms of an O,O′ atom ligating set.[11–15]

However, a recent crystallographic study[16] on a related complex obtained upon treating [Ni(acac)$_2$] with benzoyl cyanide has suggested that N,O co-ordination is also an apparent effective ligating mode for stabilizing trifunctional anionic N,O,O′ ligands to give iminocarbonylenolato complexes of the type shown (M = Ni, R = COPh). This result prompted us to reconsider the nature of the metal derivatives obtained in the reaction with cyanogen and here we present the results of an X-ray reinvestigation on β-[M(acac·C$_2$N$_2$)$_2$] (M = Ni or Cu) and on [Cu(bzacen·2C$_2$N$_2$)] (bzacen = Schiff base anion formed between ethane-1,2-diamine and benzoylacetone), together with an accurate Fourier-transform IR analysis, based on $^{13}$C labelling, of α- and β-[Ni(acac·C$_2$N$_2$)$_2$]. Further discussion on the possible structure of α-[Ni(acac·C$_2$N$_2$)$_2$] is also presented.



## Experimental

*Synthesis of the Complexes.*—The two forms (α and β) of [Ni(acac·C$_2$N$_2$)$_2$] and β-[Cu(acac·C$_2$N$_2$)$_2$] were prepared as previously reported;[11,12] the $^{13}$C-labelled nickel complexes were synthesised by reaction of anhydrous nickel acetylacetonate with $^{13}C_2N_2$ in dichloromethane, employing a slightly modified procedure. Labelled cyanogen was prepared by dropwise addition of an aqueous solution of K$^{13}$CN (1.0 g in 5 cm$^3$ of water, 99% $^{13}$C; Cambridge Isotope Laboratories) to solid CuSO$_4$·H$_2$O (1.9 g, Prolabo),[17] and was directly bubbled into a dichloromethane solution of [Ni(acac)$_2$] (0.17 g in 5 cm$^3$ CH$_2$Cl$_2$, Merck) kept at 0 °C. $^{13}$C-Labelled α-[Ni(acac·C$_2$N$_2$)$_2$] (50 mg) slowly precipitated as brittle orange microcrystals, a portion of which (30 mg) was converted into the labelled β form by heating at reflux in dichloromethane (5 cm$^3$) for 1.5 h.

*X-Ray Data Collection and Structure Determination for* β-[Ni(acac·C$_2$N$_2$)$_2$].—Suitable crystals for X-ray analysis were prepared according to ref. 11. The intensities were collected on a Philips PW 1100 four-circle diffractometer, operating in the θ–2θ scan mode, with a scan width of 1.3° and scan speed of 0.010° s$^{-1}$. The net intensities were obtained by an analysis of the profile of every reflection. The graphite-crystal monochromatized Mo-Kα radiation was employed. 1834 Independent reflections were collected up to θ = 28°; 1534 with $I > 2.5\sigma(I)$ were used in the refinement and no absorption correction was applied. The refinement of the old structural model with the new data brought down the crystallographic *R* factor to 0.048. At this point the positions of the oxygen and nitrogen atoms were exchanged according to configuration **I** (see Results and Discussion, configuration **II′** represents the starting model) and the refinement carried on. A peak close to the nitrogen position

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

**Table 1** Summary of crystal intensity collection data

| Complex | β-[Ni(acac·$C_2N_2$)$_2$] | | β-[Cu(acac·$C_2N_2$)$_2$] | | [Cu(bzacen·$2C_2N_2$)] | |
|---|---|---|---|---|---|---|
| Crystal data | $a$ = 11.369(7), $b$ = 11.555(6), $c$ = 5.919(4) Å, β = 99.1(1)°, space group $P2_1/a$, $Z$ = 2 | | $a$ = 11.460(7), $b$ = 6.112(5), $c$ = 5.611(4) Å, α = 79.5(1), β = 91.5(1), γ = 104.0(1)°, space group $P\bar{1}$, $Z$ = 1 | | $a$ = 19.863(9), $b$ = 12.184(8), $c$ = 9.739(6) Å, β = 98.4(1)°, space group $P2_1/n$, $Z$ = 4 | |
| | Previous[11] | New | Previous[13] | New | Previous[14] | New |
| Independent observed reflections | 1167 | 1534 | 1097 | — | 2272 | — |
| $R$ | 0.047 | 0.029 | 0.062 | 0.055 | 0.081 | 0.060 |
| $R'$ | 0.057 | 0.031 | 0.066 | 0.057 | 0.065 | 0.048 |
| $U_{eq}$/Å$^2$ | | | | | | |
| (M–)O *vs.* (M–)N | 0.045(2) | 0.0315(1) | 0.054(3) | 0.053(2) | 0.060(3)<br>0.052(3) | 0.053(2)<br>0.040(2) |
| (C=)N *vs.* (C=)O | 0.035(2) | 0.0536(5) | 0.040(3) | 0.062(2) | 0.065(3)<br>0.051(3) | 0.063(2)<br>0.056(2) |

was interpreted as the hydrogen and refined, without any constraint. The final N–H distance was 0.74 Å and $R$ 0.029 ($R'$ = 0.031). The weighting scheme used was 1.0/[$\sigma^2(F)$ + 0.0001$F^2$] and the highest peak in the final Fourier difference electron-density map was 0.27 e Å$^{-3}$.

*Structure Recalculation for* β-[Cu(acac·$C_2N_2$)$_2$] *and* [Cu(bzacen·$2C_2N_2$)].—The atomic coordinates of the published structure of β-[Cu(acac·$C_2N_2$)$_2$] were used as the starting model, with the only modification being the nitrogen–oxygen exchange. During the refinement a peak close to the nitrogen and with the correct values of bond distance and valence angle was interpreted as an hydrogen atom and refined. The final N–H distance was 0.89 Å and $R$ 0.055 ($R'$ = 0.057). The weighting scheme used was 1.0/[$\sigma^2(F)$ + 0.0001$F^2$]. The highest peak in the final Fourier difference electron-density map was 0.69 e Å$^{-3}$ and the highest shift/e.s.d. 0.97 : 1.

The procedure adopted for [Cu(bzacen·$2C_2N_2$)] was analogous to the previous one. The final $R$ factor was 0.060 ($R'$ = 0.048) and the N–H distances 0.88 and 0.81 Å. The highest shift/e.s.d. in the final cycle of refinement was 1.8 : 1 and the highest map residual 0.46 e Å$^{-3}$.

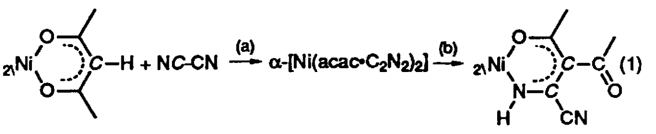
The program used for the refinement of all the structures was SHELX 76.[18] Atomic scattering factors were taken from ref. 19.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

*Infrared Spectra.*—Spectra were recorded with a Bruker IFS 66 spectrometer (resolution = 1 cm$^{-1}$) on samples prepared as KBr (4000–400 cm$^{-1}$) or crystalline polyethylene pellets (600–80 cm$^{-1}$).

## Results and Discussion

The re-evaluation, on the basis of the N,O ligating mode hypothesis, of the reported X-ray diffraction data for β-[Cu(acac·$C_2N_2$)$_2$] and [Cu(bzacen·$2C_2N_2$)] and of those newly collected for β-[Ni(acac·$C_2N_2$)$_2$] leads to a significant improvement of the $R$ factor for β-[Ni(acac·$C_2N_2$)$_2$] (0.029 *vs.* 0.047), for β-[Cu(acac·$C_2N_2$)$_2$] (0.055 *vs.* 0.062) and [Cu(bzacen·$2C_2N_2$)] (0.060 *vs.* 0.081) for (Table 1). The IR data for the three species, which were also in reasonable agreement with the O,O′ ligating mode, fit *perfectly* with the new structural interpretation and, most remarkably, the N,O ligating mode for β-[Ni(acac·$C_2N_2$)$_2$] fits with the IR data obtained from $^{13}C$ labelling. The reaction pattern of [Ni(acac)$_2$] with $C_2N_2$ has to be reformulated as in equation (1).



β-[Ni(acac·$C_2N_2$)$_2$]

Table 2 collects the most significant redetermined structural parameters for β-[M(acac·$C_2N_2$)$_2$] (M = Ni or Cu) and [Cu(bzacen·$2C_2N_2$)], together with those previously reported by us.[11,13,14] The differences in bond lengths and angles are generally small, after exchanging the position of the appropriate ring oxygen atom with that of the external NH group in the set of data referring to the previous X-ray analyses. The main changes involve the metal–nitrogen distance, which, for example, in the case of [Cu(bzacen·$2C_2N_2$)] becomes 1.918(6) instead of 1.941(8) Å, the C–N bond length in the ring, and the related angles.

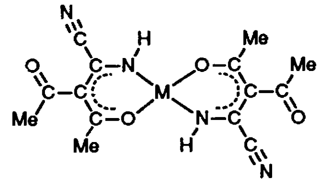
It is convenient briefly to discuss the iminoenolato complexes β-[M(acac·$C_2N_2$)$_2$] separately from the diiminato one, [Cu(bzacen·$2C_2N_2$)], the structural parameters of which are, at least in part, dictated by the rigid ligand structure.

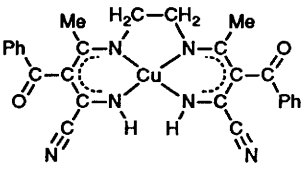
The former complexes possess a highly symmetric square-planar configuration; the extended bond delocalization through the metalloorganic ring minimizes the length differences for bonds involving different atoms such as oxygen or nitrogen. The M–O and M–N distances are very close for Ni [1.816(1) *vs.* 1.833(4) Å] and almost coincident for Cu [1.904(5) *vs.* 1.909(5) Å], whereas definite, albeit small, differences are observed for C$\cdots$O and C$\cdots$N [1.282(3) *vs.* 1.299(3) (Ni) and 1.266(6) *vs.* 1.301(6) Å (Cu)], in accordance with the larger covalent radius of nitrogen. The O–M–N(H) angle deviates from the idealized square geometry in the case of Ni [92.4(1)°], as a consequence of the smaller ionic radius of $Ni^{2+}$ (0.63 Å) compared with $Cu^{2+}$ (0.74 Å).[20]

As already noted, the reinterpretation of the data has produced the more evident effects for [Cu(bzacen·$2C_2N_2$)]; quite remarkable is the difference now between the Cu–N(H) and Cu–N($CH_2$) distances [1.918(6) *vs.* 1.953(6) Å] and the deviation of the N–Cu–N angles from 90°. Clearly, in this case, the ethylenediamine bridge plays a decisive role in determining the structural parameters. It should also be underlined that for all three complexes the bond delocalization has no structural effects on the 'external' acetyl or benzoyl substituent; in fact, (ring)C–C(=O) distances are rather long [1.477(6)–1.488(3) Å] even for a single $sp^2$–$sp^2$ C–C bond and the C=O distances are clearly ketonic in nature [1.220(9)–1.227(8) Å].[21]

The whole of these X-ray data leaves little doubt as to the N,O co-ordination to the metal centre in the β-type complexes and reopens the problem of the real nature of α-[Ni(acac·$C_2N_2$)$_2$]. In principle four configurations are possible in the solid state, as shown (carbon atoms labelled for the infrared study are italicized). They differ in the atom set co-ordinated to the metal (N,O in group **I** and O,O′ in group **II**); in particular, con-

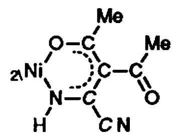
**Table 2** Selected structural parameters (bond lengths in Å, angles in °)[a]



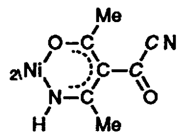


| | M | | | | [Cu(bzacen$\cdot$2$C_2N_2$)][b] | |
|---|---|---|---|---|---|---|
| | (β) Ni | (β) Ni[11] | (β) Cu | (β) Cu[13] | This work | Ref. 14 |
| M–O | 1.816(1) | 1.818(3) | 1.904(5) | 1.910(4) | | |
| M–N(H) | 1.833(4) | 1.847(3) | 1.909(5) | 1.913(3) | 1.918(6) | 1.941(8) |
| M–N($CH_2$) | | | | | 1.953(6) | 1.955(7) |
| C$\overset{\cdot\cdot}{-}$O | 1.282(3) | 1.279(4) | 1.266(6) | 1.263(6) | | |
| C$\overset{\cdot\cdot}{-}$N(H) | 1.299(3) | 1.283(4) | 1.301(6) | 1.303(6) | 1.307(8) | 1.32(1) |
| C$\overset{\cdot\cdot}{-}$N | | | | | 1.311(8) | 1.30(1) |
| C=O | 1.222(3) | 1.211(4) | 1.227(8) | 1.220(7) | 1.220(9) | 1.20(1) |
| C$\overset{\cdot\cdot}{-}$C(O) | 1.405(4) | 1.416(5) | 1.431(8) | 1.423(7) | | |
| C$\overset{\cdot\cdot}{-}$C(NH) | 1.426(3) | 1.431(4) | 1.425(8) | 1.436(7) | 1.405(9) | 1.41(1) |
| C$\overset{\cdot\cdot}{-}$C(N) | | | | | 1.434(9) | 1.43(1) |
| C–C | 1.488(3) | 1.490(4) | 1.477(6) | 1.477(7) | 1.483(9) | 1.51(1) |
| C≡N | 1.133(3) | 1.142(4) | 1.136(9) | 1.135(7) | 1.13(1) | 1.13(1) |
| O–M–NH | 92.4(1)<br>87.6(1) | 92.6(1)<br>87.4(1) | 90.2(2)<br>89.8(2) | 90.0(2)<br>90.0(2) | | |
| N–M–NH | | | | | 90.6(3) | 91.5(3) |
| N–M–N | | | | | 86.2(2) | 86.2(3) |
| HN–M–NH | | | | | 93.3(3) | 91.5(3) |
| M–O–C | 131.1(2) | 131.1(2) | 132.7(4) | 132.3(4) | | |
| M–NH–C | 127.8(2) | 127.4(2) | 127.7(4) | 127.7(4) | 127.3(5) | 125.1(7) |
| M–N–C | | | | | 129.8(4) | 130.3(6) |
| O–C–C | 123.5(2) | 123.3(3) | 123.1(6) | 123.4(5) | | |
| HN–C–C | 125.2(2) | 125.9(3) | 126.9(5) | 126.6(5) | 126.7(7) | 127.6(9) |
| N–C–C | | | | | 121.7(6) | 121.9(8) |
| C–C–C | 119.6(2) | 119.3(3) | 119.8(5) | 120.0(5) | 122.6(6) | 122.9(8) |

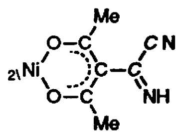
[a] The attribution of bond lengths and angles reported in the literature is modified, for clarity, by introducing the correct positions for the O and NH groups (see also text). [b] Average values; maximum individual standard deviations in parentheses.



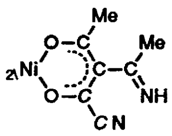
I



I′



II



II′

figuration I coincides with that found in β-[M(acac$\cdot C_2N_2)_2$] (M = Ni or Cu), **II** with that proposed so far for α-[Ni(acac$\cdot C_2N_2)_2$] and **I′** and **II′** are structures in which the positions of O and NH are mutually exchanged. The accurate infrared analysis performed in this study provides important information.

Table 3 reports all the observed bands down to 80 $cm^{-1}$, but the discussion will be focused on the aspects relevant to our configuration problem. As a general observation, the spectrum of α-[Ni(acac$\cdot C_2N_2)_2$] is similar to that of the β form, both in the position and intensity of most bands and, most remarkably, specific labelling with $^{13}C$, of the part of the ligand derived from $C_2N_2$ insertion/addition to the acetylacetonato entity, produces similar parallel shifts in the spectra of the two compounds.

It is convenient to discuss first the infrared spectrum of β-[Ni(acac$\cdot C_2N_2)_2$], because knowledge, from X-ray analysis, of its structure allows a confident attribution of the most relevant bands. The N–H stretching frequency falls at 3198 $cm^{-1}$, lower than those normally observed for organic imino groups (3350–3320 $cm^{-1}$),[22] thus indicating that nitrogen co-ordination to the metal centre produces some weakening of the N–H bond; this effect is likely emphasized by the observed intermolecular hydrogen interaction with the external keto oxygen [(N)H $\cdots$ O(C) 2.328(22) Å] (Fig. 1). The wavenumber of the C≡N stretching band is normal (2232 $cm^{-1}$) and undergoes the expected isotopic shift to 2178 $cm^{-1}$ upon $^{13}C$ labelling. The region 1650–1300 $cm^{-1}$ is characterized by very intense, fairly broad bands involving various modes of ring motions. The higher-frequency band at 1642 $cm^{-1}$, unaffected by labelling, is assigned to the C=O stretching of the external acetyl group, the very weak band at 1593 $cm^{-1}$, which becomes detectable for the labelled derivative, to a predominant C$\overset{\cdot\cdot}{-}$O stretching and the band at 1549 $cm^{-1}$ (1519 $cm^{-1}$ upon labelling) to ring vibrations with important $\nu$(C$\overset{\cdot\cdot}{-}$C) and $\nu$(C$\overset{\cdot\cdot}{-}$N) contributions.[23,24]

Moving to a consideration of the frequency range involving metal–ligand vibrations (750–80 $cm^{-1}$), a few individual assignments may be tentatively made, if one considers the literature data on metal(II) 4-iminopentan-2-onates[23] and the effect of the metal centre, resulting from the differences in the infrared spectra of the isostructural β-Ni and -Cu species. In this way the band at 475 $cm^{-1}$ is attributed to a $\nu$(M–O) mode, the three bands at 429, 384 and 349 $cm^{-1}$ to ring deformations or to metal–ligand stretchings, and the band at 286 $cm^{-1}$ to $\nu$(M–N).

The complex α-[Ni(acac$\cdot C_2N_2)_2$] shows its $\nu$(N–H) band at 3248 $cm^{-1}$, a value somewhat higher than that found for the β form, but definitely lower than those usually exhibited by unco-ordinated imino groups.[22] The C≡N stretching band falls at 2221 $cm^{-1}$ and moves to 2168 $cm^{-1}$ on $^{13}C$ labelling.

**Table 3** Infrared data (cm$^{-1}$) for [M(acac•$C_2N_2$)$_2$] (M = Ni or Cu) complexes[a]

| | α-[Ni(acac•$C_2N_2$)$_2$] | | β-[Ni(acac•$C_2N_2$)$_2$] | | |
|---|---|---|---|---|---|
| | Unlabelled | $^{13}$C Labelled | Unlabelled | $^{13}$C Labelled | β-[Cu(acac•$C_2N_2$)$_2$] |
| ν(N–H) | 3248 | 3247 | 3198 | 3198 | 3265 |
| ν(C≡N) | **2221** | **2168** | **2232** | **2178** | 2216 |
| ν(C=O) | 1634[b] | 1633[b] | 1642 | 1641 | 1632 |
| ν(C⩦O) | | 1594 | | 1593 | |
| ν(C⩦C) + ν(C⩦N) | **1548** | **1522** | **1549** | **1519** | 1551 |
| | **1461** | **1457** | **1464** | **1456** | 1471 |
| | 1446 | 1443 | 1448 | 1445 | 1458 |
| | **1420** | **1415** | **1418** | **1412** | 1420 |
| | **1390** | **1386** | **1392** | **1388** | 1398 |
| | 1364 | 1364 | 1356 | 1355 | 1365 |
| | 1352 | 1352 | | | 1342 |
| | 1302 | 1300 | 1302 | 1302 | 1300 |
| | **1191** | **1175** | **1195** | **1179** | 1178 |
| | 1069 | 1068 | 1064 | 1064 | 1065 |
| | 1064 | 1064 | | | 1036 |
| | **1037** | **1034** | **1036** | **1032** | 1030 |
| | 1014 | 1014 | 1016 | 1016 | 1019 |
| | 971 | 970 | 978 | 978 | 969 |
| | **909** | **901** | **911** | **903** | 888 |
| | 846 | 846 | 874 | 874 | 843 |
| | 735 | 730 | 730 | 730 | 737 |
| | **726** | **713** | **718** | **709** | 727 |
| | | | | | 685 |
| | 645 | 644 | 636 | 635 | 637 |
| | **604** | **594** | **610** | **605** | 606 |
| | 591 | 586 | 594 | 589 | 585 |
| | 494 | 492 | 507 | 502 | 522 |
| ν(M–O)[c] | 473 | 472 | 475 | 474 | 444 |
| ν(M–L)[c] | **433** | **427** | **429** | **425** | 402 |
| ν(M–L)[c] | **386** | **379** | **384** | **377** | 356 |
| Ring def. | 340 | 340 | 349w | 348w | 332[d] |
| ν(M–N)[c] | 298 | 298 | 286 | 285 | |
| | 267 | 266 | 253 | 252 | 250 |
| δ(L–M–L)[c] | 220 | 221 | 214 | 214 | 201 |
| δ(L–M–L)[c] | 190 | 189 | 174 | 173 | 151 |
| | 153vw | 153vw | 155vw | | 118w |
| | 106w | 105vw | | 96 | 103w |

[a] Significant isotopic shifts in bold. [b] Weak shoulder at 1643 cm$^{-1}$. [c] Tentative assignment. [d] Broad asymmetric band.

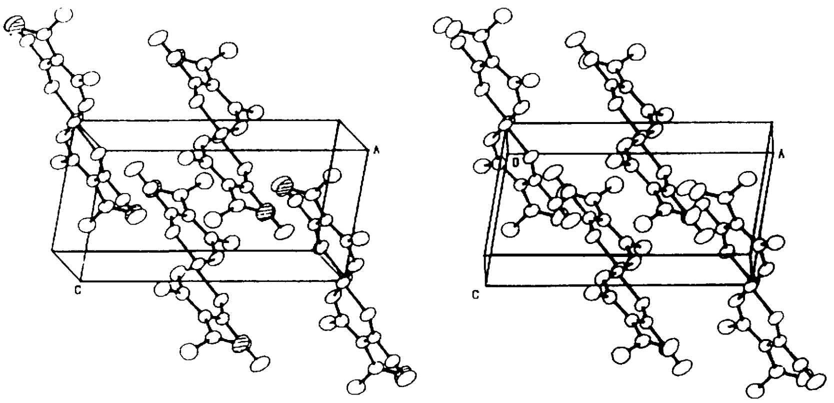


**Fig. 1** Stereographic view of the elementary cell of β-[Ni(acac•$C_2N_2$)$_2$]. The external keto oxygen atoms are indicated as crossed ellipsoids

The situation becomes more complex in the important region 1650–1300 cm$^{-1}$: there are bands at 1634 cm$^{-1}$ (with a shoulder at 1643 cm$^{-1}$), at 1548 cm$^{-1}$ and a number of bands at lower frequencies. The $^{13}$C labelling leaves the band at 1634 cm$^{-1}$ (and its shoulder) unchanged, shifts the band at 1548 to 1522 cm$^{-1}$ and slightly affects the remaining ones (4–5 cm$^{-1}$), whereas a very weak absorption emerges at 1594 cm$^{-1}$. The normally diagnostic band above 1600 cm$^{-1}$ can be attributed, on the basis of literature data,[22,24] to a C=O or to a C=NH stretching, thus making it useless for discriminating among the four possible configurations. However, the lack of any $^{13}$C labelling effect on it rules out configurations **I′** and **II**.

The choice between the remaining alternatives **I** and **II′** is not conclusive, on the basis of these spectroscopic data, although both the similarity of the spectra of the α and β forms and the impressive parallelism of the effects of $^{13}$C labelling on the individual absorption bands, especially in the 1700–700 cm$^{-1}$ region (Fig. 2), lead to the safe conclusion that the two forms possess the same N,O bonding set, *i.e.* configuration **I**.

Data in the frequency range involving metal–ligand vibrations (750–80 cm$^{-1}$) seem to support this hypothesis. There are small differences in intensity and position of the bands between the α and β forms, but the general pattern is quite similar; in particular three bands are present at 433, 386 and 340 cm$^{-1}$,

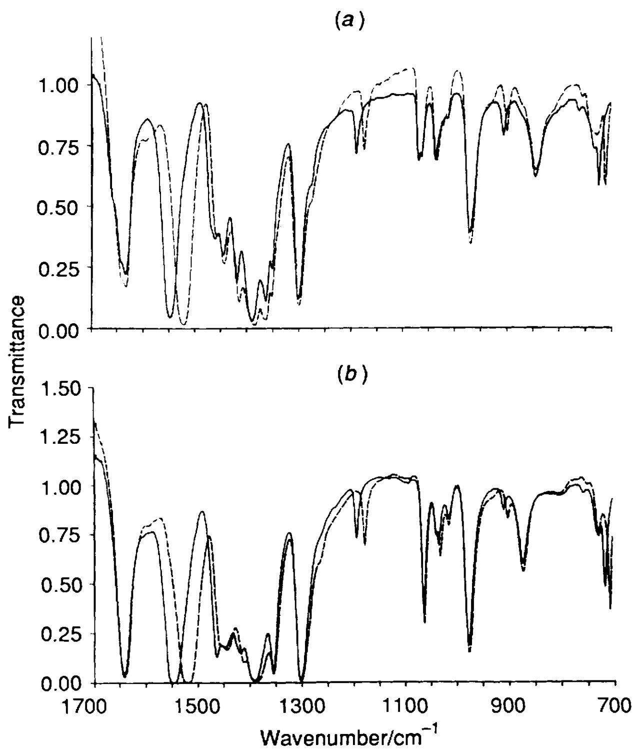


**Fig. 2** Infrared spectra (KBr pellet) of α- (*a*) and β-[Ni(acac•$C_2N_2$)$_2$] (*b*) in the 1700–700 cm$^{-1}$ region. Dashed lines correspond to the $^{13}$C-labelled derivatives

which appear indicative of an N,O bonding set; only one band is normally observed in this region for acetylacetonato-*O,O'* complexes.[23]

Analysis of the infrared spectrum of β-[Cu(acac•$C_2N_2$)$_2$] is also useful in this context: quite remarkably it is almost superimposable upon that of α-[Ni(acac•$C_2N_2$)$_2$] in most frequency regions; differences, appreciable in the position of the bands, but minimal in their relative intensities, are observed, as expected, only in the range 700–80 cm$^{-1}$, which involves metal–ligand vibrations.

Thus, on the whole, these infrared results strongly suggest that α-[Ni(acac•$C_2N_2$)$_2$] has the same configuration as that of β-[M(acac•$C_2N_2$)$_2$] (M = Ni or Cu), *i.e.* **I**, so leaving open, at the same time, the question of the observed chemical differences between the α- and β-Ni forms, as evinced, for example, by their thermal behaviour.[15] One tentative explanation is based on the observation [15] that the X-ray powder diffraction spectrum of α-[Ni(acac•$C_2N_2$)$_2$] is very similar to that of β-[Cu(acac•$C_2N_2$)$_2$] but different from that of β-[Ni(acac•$C_2N_2$)$_2$]: this indicates that the two compounds are most likely isotypic, *i.e.* that α-[Ni(acac•$C_2N_2$)$_2$] crystallizes in the same triclinic system as that of β-[Cu(acac•$C_2N_2$)$_2$], with only slightly different lattice parameters. As a consequence, it may be inferred that these two complexes not only have the same N,O bonding set, but also the overall molecular structure should be strictly similar to allow similar crystal packing. In particular, the torsion angle of the external MeC=O group with respect to the {NiNONO} plane in α-[Ni(acac•$C_2N_2$)$_2$] should have a value around 20°, close to that found in β-[Cu(acac•$C_2N_2$)$_2$] (20.7°) and different from that exhibited by β-[Ni(acac•$C_2N_2$)$_2$] (39.5°).

On these bases, it appears that the source of the differences between α- and β-[Ni(acac•$C_2N_2$)$_2$] does not lie in a diverse atom bonding set, but in the different orientations of the acetyl substituent at the metalloorganic ring. In other words, the two isolable forms of [Ni(acac•$C_2N_2$)$_2$] are, most likely, *ligand conformation isomers* and not, as previously reported,[15] *linkage isomers*.

In conclusion O,O co-ordination seems to be excluded in these iminodiketonato complexes, at least in the solid state, although we can not definitely rule out a configuration of type **II** in solution or in the gas phase, resulting from a ring opening–closure process; furthermore no convincing evidence remains for the relevance of structure **II'**, under any condition. The main spectrometric support for it was based on the electron impact and MIKE (mass-analysed ion kinetic energy) spectra of a number of [Ni(β-dik•$C_2N_2$)$_2$] (dik = diketonate) complexes: the mass loss of 42 *m/z* was attributed to the release of the diagnostic MeC=NH fragment,[25] but it can now be considered as resulting from the fragmentation of a $CH_2$=C=O moiety. As a rule, the other analytical data for these and closely related compounds reported [11–15] are also easily interpretable in the light of the results of the present investigation.

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