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Metal(II) complexes of the carbonylnitronate ligands $O_2NCHC(O)R^-$ (R = Ph, OMe or OEt) and X-ray structure of $(DMANH)[Ni(O_2NCHC(O)Ph)_3]$ (DMAN = 1,8-bis(dimethylamino)naphthalene)

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Abstract

New coordination compounds involving carbonylnitronate ligands $O_2NCHC(O)R^-$ (R = Ph, OMe or OEt) are prepared by a synthetic procedure based on the reaction of a nickel(II) or palladium(II) salt with benzoylnitromethane or alkyl nitroacetate in the presence of a deprotonating agent. The use of the proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) in tetrahydrofuran affords, in high yields, the anionic complexes $(DMANH)[Ni(O_2NCHC(O)R)_3]$ as brilliant green solids. The benzoylnitronate complex (R = Ph) crystallises in a monoclinic unit cell [space group $P2_1/n$, $a = 13.061(2)$, $b = 16.415(2)$, $c = 17.827(2)$ Å, $\beta = 102.7(2)°$], which contains four octahedral anionic nickel complexes each close to a big $DMANH^+$ cation. One nitronate ligand is easily replaced by two molecules of ethanol to give the neutral complexes $[Ni(O_2NCHC(O)R)_2(EtOH)_2]$. The nickel is *O,O′*-coordinated to the ligand through one carbonyl and one nitro oxygen atom. A different coordination mode, in which only the nitro group is bonded to the metal, is, however, observed in the palladium complexes $[PdCl(O_2NCHC(O)R)]_2$ (R = OMe, OEt). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Nickel complexes; Palladium complexes; Carbonylnitronato complexes

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1. Introduction

In the frame of our extensive work on the reactivity of C–H acid compounds towards nitriles, it has been found that the metal-catalysed C–C bond forming reaction

$$RC(O)CH_2Z + R'CN \overset{M^{n+}}{\rightarrow} RC(O)(Z)C{=}C(R')NH_2$$

is not limited to β-dicarbonyls (Z = RCO), but is also characteristic of other pronucleophiles as β-ketoamides (Z = RHNCO), β-ketophosphonates or phosphonoacetates ($Z = PO(OR)_2$) [1–3].

We have found recently that the same reaction can be extended to benzoylnitromethane and alkyl nitroacetates [4]. The nature of the catalyst (type of metal and of coordination sphere) plays an important role, as expected for a mechanism in which the first stage of the catalytic cycle is represented by coordination to the metal centre of the anion of the C–H acid substrate. The *O,O′* coordination, in which the anion acts as a bidentate ligand in a six-member chelate ring, is common with β-carbonylenolates, as shown by the very extensive studies, in particular, on the acetylacetonato complexes [5–11]. By contrast, the coordinating ability of carbonylnitronates has been checked only for the anion of α-nitroketones, with the exclusion of nitroesters [12]. This is rather surprising as, for example, Michael additions of α-nitroesters are often catalysed by transition metal centres [13,14].

In consideration of the intrinsic interest in these types of complexes and of their catalytic relevance, we report here the synthesis and characterisation of a series of new nickel(II) and palladium(II) complexes with the nitro ligands $O_2NCHC(O)R^-$ (R = Ph, OMe or OEt), having either the keto or ester function.

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2. Experimental

2.1. General

Infrared spectra were recorded on a Bruker IFS 66 FT; ^{1}H and ^{13}C NMR spectra on a Jeol FX 90Q FT or a Bruker AC (200 MHz) spectrometer. The high-resolution solid-state ^{13}C measurements were performed on a Bruker AM 250 with the setting conditions described in Ref. [15]. Thermal analyses employed the Perkin-Elmer TGS-2 equipment. The reagents were high purity products and used as received. Solvents were dried before use and the reaction apparatus carefully deoxygenated. Reactions were performed under argon at room temperature and all operations were under an inert atmosphere.

2.2. Syntheses

Synthesis of complexes $(\mathrm{DMANH})[\mathrm{Ni(O_2NCHC(O)R)_3}]$ (**1**–**3**): The starting nickel(II) compound (5 mmol, usually anhydrous $\mathrm{NiCl_2}$) was suspended in THF (30 $\mathrm{cm^3}$); the ligand $\mathrm{O_2NCH_2C(O)R}$ (7.5 mmol) and the deprotonating agent DMAN (7.5 mmol) in THF (30 $\mathrm{cm^3}$) were added dropwise and the mixture kept under stirring for 5 days. The blue by-product $(\mathrm{DMANH})_2[\mathrm{NiCl_4}]$ was filtered, the solution was concentrated and treated with ether to give the complex $(\mathrm{DMANH})[\mathrm{Ni(O_2NCHC(O)R)_3}]$ as a green solid. Shorter reaction times were needed starting from the more soluble $[\mathrm{NiCl_2(PPh_3)_2}]$; in this case the by-product was mainly $(\mathrm{DMANH})[\mathrm{NiCl_3(PPh_3)}]$.

$(\mathrm{DMANH})[\mathrm{Ni(O_2NCHC(O)Ph)_3}]$ (**1**): Green crystals, yield 95%, m.p. 189°C (Found: C, 59.00; H, 4.85; N, 9.03. $\mathrm{C_{38}H_{37}N_5NiO_9}$ requires: C, 59.5; H, 4.85; N, 9.10%). Paramagnetic, $\mu = 3.2$ BM; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3340 br [ν(N–H)], 1591 m [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1549 s, 1497 m, 1463 s, 1358 m [$\nu(\mathrm{NO_2})$], 1292 s [$\nu(\mathrm{NO_2})$], 1220 m, 976 m, 904 m, 831 w, 766 m, 706 m.

$(\mathrm{DMANH})[\mathrm{Ni(O_2NCHC(O)OMe)_3}]$ (**2**): Green crystals, yield 72%, m.p. 156°C (Found: C, 44.91; H, 5.13; N, 10.80. $\mathrm{C_{23}H_{31}N_5NiO_{12}}$ requires: C, 44.37; H, 5.13; N, 11.15%). Paramagnetic, $\mu = 3.2$ BM; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3340 br [ν(N–H)], 1630 m [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1466 s, br, 1364 m, 1306 s, 1177 s, br, 1062 s, 965 s, 840 m, 766 s.

$(\mathrm{DMANH})[\mathrm{Ni(O_2NCHC(O)OEt)_3}]$ (**3**): Green crystals, yield 66%, m.p. 157°C (Found: C, 46.58; H, 5.52; N, 10.11. $\mathrm{C_{26}H_{37}N_5NiO_{12}}$ requires: C, 46.59; H, 5.56; N, 10.54%). Paramagnetic, $\mu = 3.3$ BM; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3340 br [ν(N–H)], 1615 m [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1470 s, br, 1376 w, 1307 s, 1177 s, br, 1061 s, 966 s, 844 m, 769 s.

Synthesis of complexes $[\mathrm{Ni(O_2NCHC(O)R)_2(EtOH)_2}]$ (**4**–**6**): Complex **4** (R = Ph) was prepared by reaction of nickel acetate with benzoyl nitromethane in ethanol [12]. The same procedure gave no products with the nitroesters for which two alternative routes were used. The more straightforward one (a) implies reaction in ethanol of anhydrous nickel chloride with the nitroester and triethylamine 1:2:2 molar ratio.

$[\mathrm{Ni(O_2NCHC(O)OMe)_2(EtOH)_2}]$ (**5**): $\mathrm{NiCl_2}$ (0.31 g, 2.3 mmol) suspended in anhydrous ethanol (20 $\mathrm{cm^3}$) was treated with an ethanol solution of $\mathrm{O_2NCH_2C(O)OMe}$ (0.43 $\mathrm{cm^3}$, 4.6 mmol). To this suspension was added dropwise a solution of freshly distilled $\mathrm{Et_3N}$ (0.65 $\mathrm{cm^3}$, 4.6 mmol) in ethanol (20 $\mathrm{cm^3}$). The mixture was stirred for 3 days and the unreacted nickel chloride filtered. The resulting green solution was slowly concentrated in vacuo and the precipitate washed with ethyl ether, yield 53%, m.p. 116°C (Found: C, 31.64; H, 5.47; N, 7.39. $\mathrm{C_{10}H_{20}N_2NiO_{10}}$ requires: C, 31.04; H, 5.21; N, 7.24%). Paramagnetic, $\mu = 3.3$ BM; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3325 s [ν(O–H)], 1648 s [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1469 s, 1375 w, 1309 s, 1202 s, 1179 s, 1069 s, 966 m, 944 m, 776 s. It loses the two molecules of ethanol between 90°C and 150°C.

$[\mathrm{Ni(O_2NCHC(O)OEt)_2(EtOH)_2}]$ (**6**): $\mathrm{NiCl_2}$ (0.36 g, 2.7 mmol) suspended in anhydrous ethanol (20 $\mathrm{cm^3}$) was treated with an ethanol solution of $\mathrm{O_2NCH_2C(O)OEt}$ (0.63 $\mathrm{cm^3}$, 5.5 mmol). To this suspension was added dropwise a solution of freshly distilled $\mathrm{Et_3N}$ (0.77 $\mathrm{cm^3}$, 5.5 mmol) in ethanol (20 $\mathrm{cm^3}$). The reaction mixture was stirred for 3 days and the unreacted nickel chloride filtered. The resulting green solution was slowly concentrated in vacuo and the precipitate washed with ethyl ether, yield 65%, m.p. 112°C (Found: C, 35.06; H, 5.72; N, 6.87. $\mathrm{C_{12}H_{24}N_2NiO_{10}}$ requires: C, 34.73; H, 5.83; N, 6.75%). Paramagnetic, $\mu = 3.3$ BM; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3360 s [ν(O–H)], 1636 s [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1480 s, 1376 m, 1312 s, 1184 s, 1062 s, 953 m, 767 s. It loses the two molecules of ethanol between 90°C and 150°C.

The alternative procedure (b) involves dissolution of complexes **1**–**3** in acetone and addition of ethanol.

$[\mathrm{Ni(O_2NCHC(O)Ph)_2(EtOH)_2}]$ (**4**) and $[\mathrm{Ni(O_2NCDC(O)Ph)_2(EtOD)_2}]$ (**4-d**): Complex **1** (0.38 g, 0.50 mmol) was dissolved in the minimum quantity of acetone (15 $\mathrm{cm^3}$), then ethanol (20 $\mathrm{cm^3}$) was added causing a green precipitate of **4**, yield 96%; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 3312 s [ν(O–H)], 1591 m [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1547 s, 1500 m, 1467 s, 1438 m, 1353 m [$\nu(\mathrm{NO_2})$], 1300 s,br [$\nu(\mathrm{NO_2})$], 1226 m, 1113 w, 1049 w, 975 m, 903 m, 775 w, 701 w. The same reaction conducted by adding $\mathrm{C_2H_5OD}$ gave the deuterated complex **4-d**; $\tilde{\nu}_{\max}/\mathrm{cm^{-1}}$ (KBr) 2431 m [ν(O–D)], 1589 m [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 1546 s, 1447 m, 1385 s, br, 1356 m [$\nu(\mathrm{NO_2})$], 1284 s [$\nu(\mathrm{NO_2})$], 1172 m, 1050 w, 966 m, 924 m, 873 w, 701 w.

$[\mathrm{Ni(O_2NCHC(O)OMe)_2(EtOH)_2}]$ (**5**) and $[\mathrm{Ni(O_2NCHC(O)OEt)_2(EtOH)_2}]$ (**6**): Complex **2** (or **3**) (0.5 mmol) was dissolved in ethanol (5–10 $\mathrm{cm^3}$) and diethyl ether (20 $\mathrm{cm^3}$) was slowly added. The slow crystallisation (few days) afforded small green crystals of **5** (yield 30%) (or of **6**, yield 40%).

Synthesis of complex $[\mathrm{Pd(O_2NCHCOPh)_2}]$ (**7**): This complex was prepared by extending to palladium a reported procedure [12], using acetone instead of ethanol as solvent. Palladium acetate (0.23 g, 1.0 mmol) and $\mathrm{O_2NCH_2COPh}$

were dissolved in dry acetone (20 cm^3) and left under stirring for 20 h. The volume was reduced in vacuo and the yellow–brown precipitate washed with diethyl ether, yield 72%, m.p. (dec.) 171°C (Found: C, 44.11; H, 2.75; N, 6.37. $C_{16}H_{12}N_2O_6Pd$ requires: C, 44.21; H, 2.78; N, 6.44%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1596 m and 1586 m [ν(C≐O)], 1511 s, 1468 s, 1393 s [$\nu(NO_2)$], 1264 s [$\nu(NO_2)$], 1228 m, 1186 w, 1101 w, 1000 w, 942 m, 916 m, 774 w, 694 w; δ_H (DMSO-d_6) 6.30 and 6.54 (s, 1H, C*H*), 7.3–8.1 (m, 5H, Ph); δ_C (solid state) 116.3 (*C*H), 128.6, 130.6 and 136.4 (Ph), 183.9 (*C*≐O).

Synthesis of complexes $[PdCl(O_2NCHC(O)R)]_2$ (**8, 9**): They were prepared by reaction of anhydrous palladium chloride with $K(O_2NCHC(O)R)$ in THF.

$K(O_2NCHC(O)R)$: An equimolar quantity of the nitro ester $O_2NCH_2C(O)R$ and of potassium metal were suspended in anhydrous THF, under vigorous stirring at 25°C. After ca. 3 days the potassium disappeared and the resulting white suspension was filtered. The product was never dried, because, carbonylnitronates of alkali metals are potentially explosive [16]. They were identified from their infrared spectra; $K(O_2NCHCOOMe)$: $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1676 s [ν(CO)], 1452 s, br, 1279 s, 1142 s, 1071 s, 766 m; $K(O_2NCHCOOEt)$: $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1686 s [ν(CO)], 1472 s, br, 1291 s, 1148 s, 1071 s, 770 m.

$[PdCl(O_2NCHC(O)OMe)]_2\cdot 0.2THF$ (**8**): $[PdCl_2(PhCN)_2]$ (0.76 g, 2.0 mmol) in THF (15 cm^3) was treated with a solution of $K(O_2NCHCOOMe)$ (0.69 g, 4.0 mmol) in THF. The mixture was left under stirring at room temperature for 4 days and traces of palladium metal filtered. The red–brown solution was evaporated to dryness and the resulting yellow–brown solid crystallised from THF–ether, yield 95%, m.p. (dec.) 146°C (Found: C, 16.92; H, 1.83; N, 5.27. $C_{3.8}H_{5.6}ClNO_{4.2}Pd$ requires: C, 16.64; H, 2.06; N, 5.11%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1720 s [ν(C=O)], 1620 w, 1564 w, 1515 s, 1466 m, 1436 m, 1340 s, 1176 s, 1067 m, 907 w; far infrared (in Nujol, cm^{-1}): 330 br; δ_H (DMSO-d_6) 3.60 (s, 3H, CH_3O), 2.81 (s, 1H, C*H*); δ_C (solid state) 54.2 (*C*H_3O), ca. 67 (*C*H), 69.4 (THF), 172.0 (CO). It explodes violently at temperatures above 146°C.

$[PdCl(O_2NCHC(O)OEt)]_2$ (**9**): Anhydrous $PdCl_2$ (0.36 g, 2.0 mmol) suspended in THF (20 cm^3) was treated with a solution of $K(O_2NCHCOOEt)$ (0.69 g, 4.0 mmol) in THF. The reaction mixture was left under stirring at room temperature for 4 days and the unreacted $PdCl_2$ filtered off. The red–brown solution was evaporated to dryness and the resulting yellow–brown solid crystallised from THF–ether, yield 85%, m.p. 143°C (Found: C, 17.71; H, 2.14; N, 4.97. $C_4H_6ClNO_4Pd$ requires: C, 17.54; H, 2.21; N, 5.11%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1714 s [ν(C=O)], 1616 w, 1565 m, 1516 s, 1472 m, 1324 s, 1187 s, 1092 m, 1033 m, 911 w, 863 w; far infrared (in Nujol, cm^{-1}): 330 br; δ_H (DMSO-d_6) 1.24 (t, 3H, CH_3CH$_2$O), 4.14 (q, 2H, CH$_3$CH_2O), 2.81 (s, 1H, C*H*); δ_C (solid state) 17.4 (*C*H$_3$CH$_2$O), 62.9 (CH$_3$*C*H$_2$O), ca. 67 (*C*H), 173.0 (CO). It explodes violently at temperatures above 143°C.

2.3. X-ray crystal structure determination of (DMANH)[Ni(O$_2$NCHC(O)Ph)$_3$]

Suitable crystals of **1** were obtained by slow crystallisation at 4°C from a solution in acetone. The X-ray work was carried out on a Philips four-circle diffractometer with monochromatic Mo Kα radiation. Crystal data: $C_{38}H_{37}N_5NiO_9$, $M = 766.45$, $F(000) = 1600$, monoclinic, space group $P2_1/n$, $a = 13.061(2)$, $b = 16.415(2)$, $c = 17.827(2)$ Å, $\beta = 102.7(2)°$, $V = 3728(3)$ Å^3, $D_c = 1.37$ g cm^{-3}, $Z = 4$, λ(Mo Kα) = 0.71069 Å, $\mu = 5.79$ cm^{-1}. Intensities were measured by the θ–2θ method up to $\theta = 28°$ yielding 8291 unique reflections of which 2702 were significantly above background [$F > 4\sigma(F)$]. The structure was solved by a direct method using the SIR 92 program [17]. The positions of the C, N, O and Ni atoms were refined with cycles of blocked least-squares using thermal anisotropic parameters. All hydrogen atoms were identified in the difference Fourier map and introduced with isotropic thermal parameters in the final refinement cycles (SHELX 76). Convergence was reached at $R = 0.071$ and $R_w = 0.069$ ($w = 1/[\sigma^2(F) + 0.001154\,F^2]$).

3. Results and discussion

The reaction of a metal(II) salt with benzoylnitromethane or alkyl nitroacetates gives, in the presence of a deprotonating agent, complexes in which the monoanion of the nitro derivative is coordinated to the metal centre. The success of the synthesis and the nature of the obtained complexes markedly depend on many variables: the metal centre, the nitro pronucleophile, the base.

The proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) proved to be very efficient in reactions with nickel chloride. In nonalcoholic solvents, as tetrahydrofuran, the anionic complexes (DMANH)[Ni(O$_2$NCHC(O)R)$_3$] **1**–**3** are obtained in good yield, according to Eq. (1).

$$\begin{aligned}&2NiCl_2 + 3O_2NCH_2C(O)R + 3DMAN\\&\quad\rightarrow (DMANH)[Ni(O_2NCHC(O)R)_3]\ (\mathbf{1}\text{–}\mathbf{3})\\&\qquad + (DMANH)_2[NiCl_4]\end{aligned}\tag{1}$$

R = Ph (**1**); OMe (**2**); OEt (**3**)

So DMAN not only efficiently deprotonates the nitro carbonyl $O_2NCH_2C(O)R$, but also acts, in its protonated form, as countercation. The efficiency of the synthesis is due, at least in part, to the formation of (DMANH)$_2$[NiCl$_4$] as by-product, which is almost insoluble in the reaction medium and drives the reaction towards the products. The molecular structure of the complex (DMANH)[Ni(O$_2$NCH-C(O)Ph)$_3$] (**1**) shows an octahedral geometry around the metal centre. The benzoylnitronate moiety is coordinated to the nickel(II) through one keto and one nitro oxygen atom (Fig. 1). The planarity of the ligand (excluding the phenyl substituent) and the bond distances (Tables 1 and 2, average values: Ni–O 2.02, C≐O 1.24, C≐C 1.40, C≐N 1.38, N≐O

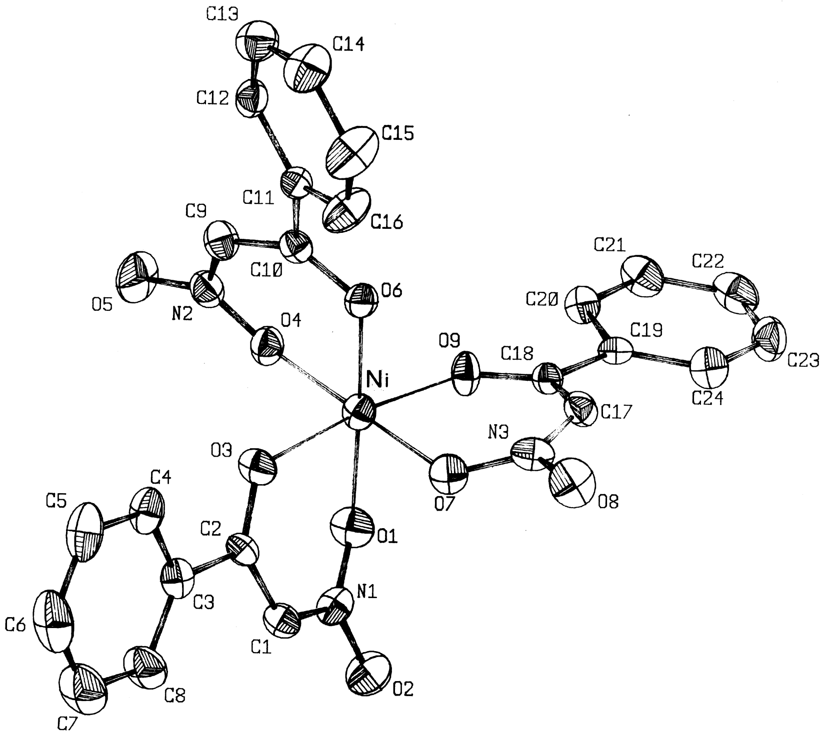


Fig. 1. ORTEP view of the anionic complex $[Ni(O_2NCHC(O)Ph)_3]^-$.

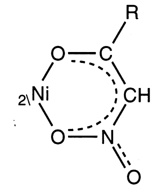
1.27, N=O 1.23 Å) clearly indicate that electron delocalisation involves all bonds.

These distances can be compared with those reported for: $[Cu(O_2NCHC(O)Ph)_2]$ and its adducts with 2- and 4-methylpyridine [18], *cis*-dipyridine complexes of $[Zn(O_2NCHC(O)Ph)_2]$ and $[Mn(O_2NCHC(O)Ph)_2]$ [19,20], and other chelate complexes having nitro and keto groups as $Ag[Ni(acac)_3]\cdot 2AgNO_3\cdot H_2O$ [21], *trans*-$[Pd(bzac)_2]$ [22], *cis*-$[Pd(bzac)_2]$ [23,24], *trans*-$[Cu(bzac)_2]$ [25], $K_2[Cu(O_2NCHCOO)_2]\cdot H_2O$ [26], $[Ni(O_2NCHCOO)N_4]$ (N_4 = cyclic tetradentate ligand) [27], $(C_5H_5)Zr(Cl)[O_2N{=}C(CH_3)_2]$ [28], $[Li(O_2N{=}CHPh)\cdot EtOH]_n$ [29].

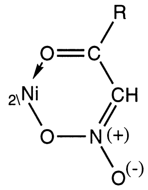
Table 1
Selected bond distances (Å) for **1**

Ni–O(1)	2.046(7)	Ni–O(3)	2.011(5)
Ni–O(4)	2.030(6)	Ni–O(6)	1.996(6)
Ni–O(7)	2.019(6)	Ni–O(9)	2.016(6)
O(1)–N(1)	1.27(1)	O(2)–N(1)	1.24(1)
O(3)–C(2)	1.24(1)	O(4)–N(2)	1.28(1)
O(5)–N(2)	1.23(1)	O(6)–C(10)	1.25(1)
O(7)–N(3)	1.275(9)	O(8)–N(3)	1.23(1)
O(9)–C(18)	1.236(9)	N(1)–C(1)	1.36(1)
N(2)–C(9)	1.41(1)	N(3)–C(17)	1.38(1)
N(4)–C(25)	1.45(1)	N(4)–C(35)	1.50(1)
N(4)–C(36)	1.47(1)	N(5)–C(31)	1.48(1)
N(5)–C(37)	1.49(1)	N(5)–C(38)	1.50(1)
C(1)–C(2)	1.42(1)	C(2)–C(3)	1.504(9)
C(9)–C(10)	1.38(1)	C(10)–C(11)	1.51(1)
C(17)–C(18)	1.41(1)	C(18)–C(19)	1.501(9)
C(25)–C(26)	1.37(1)	C(25)–C(30)	1.44(1)
C(26)–C(27)	1.39(2)	C(27)–C(28)	1.36(1)
C(28)–C(29)	1.41(1)	C(29)–C(30)	1.42(1)
C(29)–C(34)	1.41(1)	C(30)–C(31)	1.43(1)
C(31)–C(32)	1.36(1)	C(32)–C(33)	1.41(1)
C(33)–C(34)	1.35(1)		

It is seen that the average C–O bond length (1.24 Å) in **1** is slightly shorter than in the Cu (1.27), Zn (1.25) and Mn (1.25 Å) benzoylnitronates. Furthermore, the observed value is lower than that reported in benzoylacetonato complexes (1.29 Å); thus it appears that the nitro group favours, compared with the acetyl, an enhanced double bond character of the benzoyl carbonyl (typical value for $C(sp^2){=}O$ 1.21 Å) [30,31]. The N–O distance for the metal-coordinated oxygen has a value (1.27 Å) between that found in organic nitro compounds (1.22 Å) [31] and in alkanenitronate complexes (1.30–1.34 Å, N–O single bond) [28,29]. At the same time, the N–O bond for the oxygen not involved in coordination maintains a high degree of double bond character (1.23 Å). Thus the chelate ring can be sketched as in (a), whereas (b) and (c) represent the two more important limit forms (R = Ph).



a)



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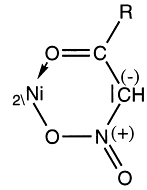


c)

Table 2
Selected bond angles (°) for **1**

O(7)–Ni–O(9)	88.5(3)	O(6)–Ni–O(9)	94.7(3)
O(6)–Ni–O(7)	90.1(2)	O(4)–Ni–O(9)	93.4(3)
O(4)–Ni–O(7)	177.0(3)	O(4)–Ni–O(6)	87.3(3)
O(3)–Ni–O(9)	172.7(3)	O(3)–Ni–O(7)	88.6(2)
O(3)–Ni–O(6)	92.0(2)	O(3)–Ni–O(4)	89.9(3)
O(1)–Ni–O(9)	87.2(3)	O(1)–Ni–O(7)	90.6(3)
O(1)–Ni–O(6)	178.0(3)	O(1)–Ni–O(4)	91.9(3)
O(1)–Ni–O(3)	86.1(3)	Ni–O(1)–N(1)	123.5(5)
Ni–O(3)–C(2)	125.1(5)	Ni–O(4)–N(2)	125.9(5)
Ni–O(6)–C(10)	123.8(6)	Ni–O(7)–N(3)	126.0(6)
Ni–O(9)–C(18)	126.7(5)	O(1)–N(1)–O(2)	117.8(8)
O(2)–N(1)–C(1)	118.2(9)	O(1)–N(1)–C(1)	124.0(8)
O(4)–N(2)–O(5)	119.8(8)	O(5)–N(2)–C(9)	120.1(9)
O(4)–N(2)–C(9)	120.1(8)	O(7)–N(3)–O(8)	117.6(9)
O(8)–N(3)–C(17)	120.2(8)	O(7)–N(3)–C(17)	122.0(8)
C(35)–N(4)–C(36)	109.1(7)	C(25)–N(4)–C(36)	112.4(8)
C(25)–N(4)–C(35)	111.8(6)	C(37)–N(5)–C(38)	112.1(8)
C(31)–N(5)–C(38)	114.1(6)	C(31)–N(5)–C(37)	111.2(7)
N(1)–C(1)–C(2)	123.8(9)	O(3)–C(2)–C(1)	126.2(8)
C(1)–C(2)–C(3)	116.7(8)	O(3)–C(2)–C(3)	117.1(7)
C(2)–C(3)–C(8)	123.0(6)	C(2)–C(3)–C(4)	117.0(7)
N(2)–C(9)–C(10)	126.1(9)	O(6)–C(10)–C(9)	127.0(8)
C(9)–C(10)–C(11)	115.7(7)	O(6)–C(10)–C(11)	117.2(7)
C(10)–C(11)–C(16)	117.2(6)	C(10)–C(11)–C(12)	122.7(6)
N(3)–C(17)–C(18)	127.1(9)	O(9)–C(18)–C(17)	124.5(8)
C(17)–C(18)–C(19)	117.7(7)	O(9)–C(18)–C(19)	117.8(7)
C(18)–C(19)–C(24)	123.0(5)	C(18)–C(19)–C(20)	117.0(6)
N(4)–C(25)–C(30)	119.0(8)	N(4)–C(25)–C(26)	122.2(8)
C(26)–C(25)–C(30)	118.7(8)	C(25)–C(26)–C(27)	122.7(9)
C(26)–C(27)–C(28)	120(1)	C(27)–C(28)–C(29)	121.0(9)
C(28)–C(29)–C(34)	120.3(8)	C(28)–C(29)–C(30)	119.4(8)
C(30)–C(29)–C(34)	120.2(8)	C(25)–C(30)–C(29)	118.4(8)
C(29)–C(30)–C(31)	116.8(7)	C(25)–C(30)–C(31)	124.8(8)
N(5)–C(31)–C(30)	120.2(7)	C(30)–C(31)–C(32)	121.5(8)
N(5)–C(31)–C(32)	118.4(8)	C(31)–C(32)–C(33)	120.2(8)
C(32)–C(33)–C(34)	120.6(8)	C(29)–C(34)–C(33)	120.7(8)

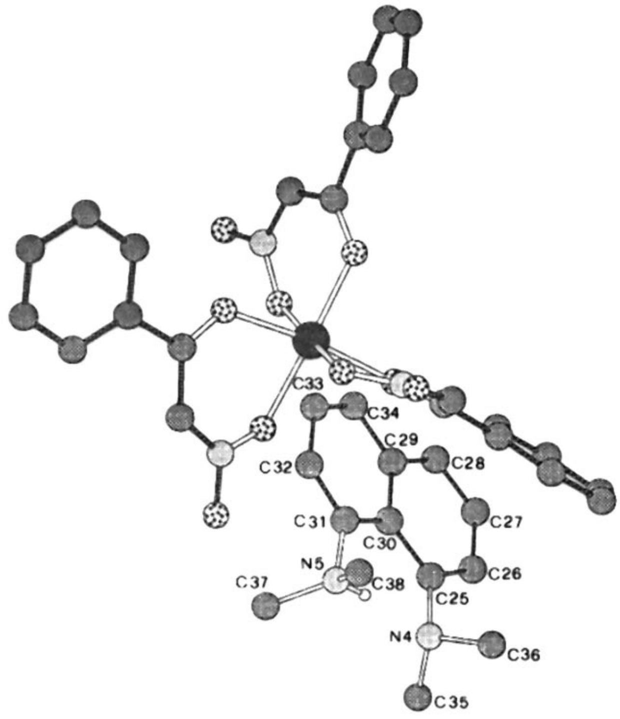


Fig. 2. View of complex **1** including the countercation DMANH$^+$.

The importance of structure (c) in which a negative charge is localised on the methine carbon supports our mechanistic proposals on the metal-catalysed C–C bond forming reaction between C–H acid nitro derivatives and nitriles [4].

The deprotonating agent DMAN is not only a strong base (pK_a 12) [32,33], but also a very hindering molecule and the big cation, which is formed during the reaction, can favour the crystallisation of complex **1**. Fig. 2 shows that, albeit in the absence of definite bond interactions, the protonated base lies rather close to the anionic complex, thus stabilising the crystal structure. As a matter of fact the use of other deprotonating agents like TlOEt or K metal gives intractable mixtures. The bond distances and angles in DMANH$^+$ are very similar to those found in DMANH$^+$ClM$^-$ (ClMH = 1,2-dichloromaleic acid) [34–36] and, in particular, the cation is characterised by an unsymmetrical N–H···N hydrogen bond, whose geometric parameters [N–H = 0.80(1), N···H = 1.86(1) Å, N–H···N = 168.7(5)°] fit well with ab initio calculations [34].

The infrared spectrum of **1** is consistent with the molecular structure determined by X-rays and shows, in particular, a band at 1591 cm^{-1} attributable to the coordinated carbonyl [10,15], which can be compared with that at 1700 cm^{-1} found in the free ligand. The identification of the NO_2 stretching bands is less reliable, but it may be proposed on the basis of the deuteration test made on complex **4** (see later); thus the asymmetric and symmetric stretching bands of the ligand at 1555 and 1330 cm^{-1} become in the complex two bands at 1358 and 1292 cm^{-1} corresponding to the N–O stretching of the uncoordinated and coordinated oxygen. The marked shift to lower wavenumber for both the carbonyl and nitro groups is indicative of a reduction of their double bond character as a consequence of coordination to the metal.

Complexes (DMANH)[Ni($O_2NCHC(O)R)_3$] (**2**) (R = OMe) and **3** (R = OEt), derived from methyl and ethyl nitroacetate respectively, are also easily obtained in good yield as green microcrystals. Their infrared spectra show coordination of the carbonyl oxygen of the ester; in fact the CO stretching frequency moves from 1755 to 1630 (**2**) and from 1755 to 1615 (**3**) [37]. The two medium intensity bands of the nitro group in the free ligand at 1563 (**2**), 1563 (**3**) and 1343 (**2**), 1335 (**3**) are absent in the complexes and no absorptions are observable between 1630 and 1480 cm^{-1}. Thus, despite the difficulty of a safe attribution for the NO_2 stretchings in the absence of labelling experiments, they surely have moved to lower energies, supporting for complexes **2**, **3** the same type of coordination to the metal, via one carbonyl and one nitro oxygen atom, fully demonstrated for the ω-nitroacetophenonates.

Complexes [Ni($O_2NCHC(O)R)_2(EtOH)_2$] (**4**–**6**) can be synthesised in more than one way; a clear distinction has to be made between the keto and the ester nitro derivatives. It has been reported that **4** (R = Ph) and the analogous ML_2 complexes of various bivalent transition metals (M = Mn, Fe, Co, Ni, Cu, Zn) are easily obtained by reaction of their acetates with benzoylnitromethane in ethanol [12]. This procedure cannot be extended to the synthesis of the nitroester complexes **5** (R = OMe) and **6** (R = OEt); in fact, the reacting nickel acetate and the ester are recovered unchanged after 4 h at reflux in ethanol. Thus, the reaction is better carried out using anhydrous nickel chloride in the presence of a base like triethylamine to deprotonate the nitroacetate (Eq. (2)).

$$\mathrm{NiCl_2 + 2O_2NCH_2C(O)R + 2Et_3N} \xrightarrow{\mathrm{EtOH}} \mathrm{[Ni(O_2NCHC(O)R)_2(EtOH)_2] + 2(Et_3NH)Cl} \qquad (2)$$

Complexes **4–6** are also obtained by dissolving **1–3** in acetone or dichloromethane and treating them with ethanol to displace one carbonylnitronate ligand (Eq. (3)). Treatment with water gives extended hydrolysis of the coordinated ester.

$$\mathrm{(DMANH)[Ni(O_2NCHC(O)R)_3]}\ (\mathbf{1}\text{–}\mathbf{3}) + \mathrm{2EtOH} \rightarrow \mathrm{[Ni(O_2NCHC(O)R)_2(EtOH)_2]}\ (\mathbf{4}\text{–}\mathbf{6}) + \mathrm{(DMANH)(O_2NCHC(O)R)} \qquad (3)$$

The easy replacement by ethanol would indicate that these anionic bidentate ligands have moderate bonding ability, at least with ester substituents, whereas in the case of benzoylnitromethane the substitution may be favoured by the limited solubility of **4**.

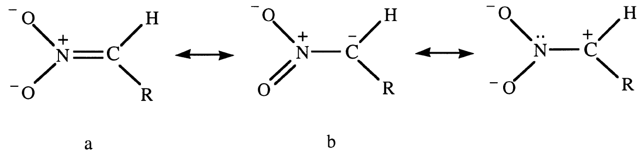
Complex **1**, when treated with C_2H_5OD, gives $[Ni(O_2NCDC(O)Ph)_2(EtOD)_2]$ (**4-d**), as the result of an H/D exchange involving the methine hydrogen. Comparison of the infrared spectra of **4** and **4-d** shows, in particular, that in the region 1600–1200 cm^{-1} only the bands at 1353 and 1300 cm^{-1} are scarcely affected by the deuteration, so being attributable to the two NO stretchings. This hypothesis is confirmed by a similar study on the square planar $[Cu(O_2NCDC(O)Ph)_2]$ [4]. The spectra of complexes **4–6** show the expected bands at 1591 (**4**), 1648 (**5**), 1636 (**6**) cm^{-1} of the coordinated carbonyl and are similar, as a whole, to those of the corresponding complexes **1–3**, so it is easy to envisage the same type of *O*,*O′* coordination via CO and NO_2 oxygen atoms.

The diamagnetic square planar palladium complex $[Pd(O_2NCHC(O)Ph)_2]$ (**7**) can be prepared in acetone from palladium acetate by an extension of the reported procedure [12]. Its infrared spectrum is characterised by two bands at 1596 and 1586 cm^{-1} attributable to the CO stretching of the coordinated carbonyl (*cis* and *trans* isomers) and by the bands relative to the NO_2 group at 1393 and 1264 cm^{-1}. The NMR data are particularly interesting because they give novel information on a coordinated carbonylnitronate moiety. The values of 6.30 and 6.54 ppm for the methine hydrogen can be compared with the values of 6.06 and 6.04 found in *cis*- and *trans*-$[Pd(MeC(O)CHC(O)Ph)_2]$ [24]; a marked shift to lower field is also observed for the ^{13}C CH resonance [116.3 versus 98.4 (*cis*) and 98.6 (*trans*) ppm]. These data indicate that the methino group has an increased vinylic character and that the benzoyl and nitro substituents exhibit a strong deshielding effect. The carbonyl resonance at 183.9 ppm has a lower chemical shift with respect to organic carbonyls (ca. 200 ppm) [38] and also to benzoyl carbonyls coordinated to palladium [188.4 (*cis*) and 188.6 (*trans*)], thus indicating an enhanced reduction of the double C=O bond [15].

Attempts to prepare the ester complexes analogous to **7** by reaction of palladium acetate with the nitro ligands in ethanol were unsuccessful, because of an extensive hydrolysis of the ester group. Coordination of the carbonylnitronate ligand $O_2NCHC(O)R^-$ (R = OMe, OEt) is achievable under very anhydrous conditions by reaction in THF of $PdCl_2$ (or $[PdCl_2(PhCN)_2]$) with $K(O_2NCHC(O)R)$. This synthetic procedure gives complexes of formula $[PdCl(O_2NCHC(O)R)]_2$, in which only one chlorine atom has been replaced by the carbonylnitronate.

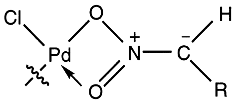
The bands at 1720 (**8**) and 1714 (**9**) cm^{-1} are attributable to the stretching of an uncoordinated ester carbonyl. These values are only slightly lower (ca. 30 cm^{-1}) than in the free ligand, so coordination to the metal has to be ruled out, because, as reported [37] and observed in complexes **2**, **3**, **5** and **6**, the resulting reduction of the double bond character in C=O would give stretching values slightly above 1600 cm^{-1}. On the other hand a small energy decrease is expected anyway, because of weak electron delocalisation in the coordinated anionic ligand extended to all functional groups. The attribution for the NO_2 stretching bands [1340 and 1176 (**8**), 1324 and 1187 (**9**) cm^{-1}] is tentative, as no well defined values are reported in the literature [39], and would imply for the coordinated nitro group shifts to lower energy of ca. 230 and ca. 150 cm^{-1}. In addition one broad band is observed at ca. 330 cm^{-1} in the far IR attributable to a Pd–Cl stretching in bridged complexes [40].

The NMR spectra were obtained in deuteroacetone solutions for the proton and in the solid state for ^{13}C, because the limited stability in solution of complexes **8** and **9** is incompatible with the accumulation times required for ^{13}C. The methino group shows the proton resonance at 2.81 (**8** and **9**); this value is completely different from that observed in **7** (6.30 and 6.54 ppm). Also the ^{13}C resonance [ca. 67 (**8**) and (**9**)] occurs at much higher fields, thus suggesting a different coordination mode. The ^1H and ^{13}C signals of the C–H group are fairly close to those of organic nitroacetates, suggesting in particular that the carbon maintains an sp^3 hybridization. The alkanenitronate anion can present more limit formulas whose weight depends on the various substituents and type of coordinated metal.



It has been observed that the first limit formula (a) is important with complexes of Cu(I) [39], Ni(II) [41], and Zr(IV) [28]; in fact, in this last case, the CH proton resonates at 6.10 ppm and the carbon at 112.85 ppm. By contrast, with complexes **8** and **9** it seems reasonable to propose a coordination in which the C–N bond is almost single and the carbon pseudotetrahedral as in (b).

The palladium(II) metal centre should complete the coordination sphere by forming a Cl-bridged dimer.



Attempts to extend the synthesis of nitroester complexes to other metal centres were unsuccessful. Co(II) and Cu(II) acetates do not react with nitroesters in ethanol at reflux for hours. In the case of copper(II) many alternative ways were attempted by reacting $CuCl_2$ with: (i) $O_2NCH_2C(O)R$ (R = OMe, OEt) in the presence of various bases (pyridine, triethylamine, sodium ethoxide) or of potassium metal; (ii) $K(O_2NCHC(O)R)$. In all cases only carboxylato complexes resulting from the hydrolysis of the ester group could be identified.

In conclusion, we have found a good general method for the synthesis of homoleptic octahedral nickel complexes of the type $(DMANH)[Ni(O_2NCHC(O)R)_3]$ (R = Ph, OMe, OEt), where the big protonated base acts as countercation to stabilise the crystal structure. The bidentate carbonylnitronato ligand is *O*,*O*′-coordinated to the metal centre via the carbonyl and the nitro group. Proper conditions allow also the synthesis of the neutral nickel complexes $[Ni(O_2NCHC(O)R)_2(EtOH)_2]$, in which one anionic ligand has been replaced by two molecules of ethanol. The extension of this coordination chemistry to other metal centres is easy only for benzoylnitromethane whereas, with methyl and ethyl nitroacetates, metal-catalysed hydrolysis of the ester group is often observed. The reduced bonding ability of the ester carbonyl in these ligands is outlined by the synthesis of palladium complexes $[PdCl(O_2NCHC(O)R)]_2$, in which only the nitro group is coordinated to the metal.

4. Supplementary material

Complete tables of fractional coordinates of all atoms, bond distances and bond angles, anisotropic thermal parameters and observed and calculated structure factors for **1** may be obtained from author M.B.

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