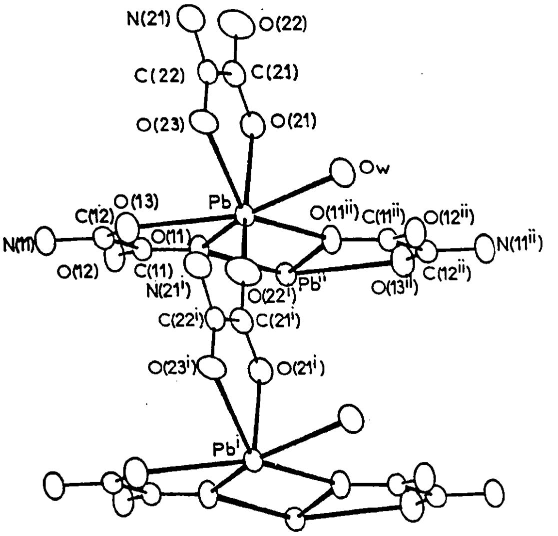

Fig. 2. Part of the polymeric 'double chain', showing the atom labelling.

lengths are in the range 2·489–2·662 Å. There is a distortion of the basal atoms away from O(22) and towards O(21): all O(21)—Pb—O (basal) angles, with the exception of O(21)—Pb—O(13) (Table 2), are <90°. This feature is also observed in other cases and can be explained by the assumption that the stereochemically active lone pair of Pb is directed towards O(22) and pushes all O atoms to the other side of the metal atom (Rajaram & Mohana Rao, 1982; Clegg, Little & Straughan, 1986).

The geometry of the oxamate ions is not unusual (Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1972; Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Skoulika, Michaelides & Aubry, 1988). The two oxamates of the asymmetric unit fill different structural roles. One is tridentate and ensures, by the coordination of its second carboxylic O atom O(22) to Pb, the formation of polymeric chains parallel to **a**. The second oxamate ion is bidentate and, by bridging, through O(11), two Pb atoms related by the center of symmetry, permits the interaction between two parallel chains and the formation of 'double chains' (Fig. 2). The Pb_2O_2 parallelograms formed in this way are almost coplanar with the oxamate ions containing the O atoms (distance of the Pb atoms from the mean plane of the two oxamates −0·323 and 0·257 Å).

The water molecule that is coordinated to Pb is also involved in three hydrogen bonds. For this purpose it uses both H atoms to form hydrogen bonds to two O atoms of the oxamate ions and acts as acceptor in an additional hydrogen bond to an N atom. By means of these interactions the 'double chains' are hydrogen bonded between them and the overall structure of the hydrate stabilized.

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Structure of (2,2'-Bipyridyl)carbonyl(η-3,4-diphenylcyclobutene-1,2-dione)nickel(0) Toluene Solvate

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Abstract. $[Ni(C_{10}H_8N_2)(C_{16}H_{10}O_2)(CO)].0{\cdot}5C_7H_8$, $M_r = 523{\cdot}3$, monoclinic, $P2_1/a$, $a = 15{\cdot}230\,(4)$, $b = 9{\cdot}489\,(2)$, $c = 17{\cdot}652\,(2)$ Å, $\beta = 96{\cdot}95\,(1)^\circ$, $V = 2532{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}38$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}80$ mm^{-1}, $F(000) = 1084$, $T = 291$ K. Final $R = 0{\cdot}056$ ($wR = 0{\cdot}066$) for 1992 unique observed reflections. The cyclobutenedione ring is coordinated to the Ni atom *via* its olefinic bond, with the plane of the cyclobutene ring making an angle of 87° to that of the three-membered ring defined by the

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C=C bond and the Ni atom. The crystal contains a disordered solvent molecule.

Introduction. (2,2′-Bipyridyl)(1,4-dioxo-2,3-diphenyl-2-butene-1,4-diyl)nickel reacts reversibly with carbon monoxide to form the title compound (Hoberg & Herrera, 1981), where a rearrangement of the five-membered ring and the formation of a cyclobutenedione ring π-bonded to an Ni atom have occurred. In principle, cyclobutenedione has six π electrons available for donation to the Ni atom. However, only two of these are required by the Ni atom to complete its 18 e configuration. The structure of the compound was determined in order to establish how the cyclobutenedione ring is attached to the Ni atom. A preliminary report of the structure was given with the preparative work (Hoberg & Herrera, 1981). (1-Methyl-2-phenylcyclobutenedione)bis(triphenylphosphine)platinum(0) (Russell & Tucker, 1976) is the only other example of a structurally characterized compound containing a cyclobutenedione ring bonded to a transition metal. Here we give a detailed description of the structure of the Ni complex and a comparison of the two structures.

Experimental. The preparation of the title compound has been described by Hoberg & Herrera (1981). Crystals were grown as red-brown prisms from toluene solution. The crystal chosen for data collection was 0·15 × 0·17 × 0·24 mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 75 automatically centred reflections ($6{\cdot}4 \leq \theta \leq 17{\cdot}0°$). Intensity data were measured within the range $1{\cdot}16 \leq \theta \leq 25{\cdot}9°$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ X-radiation by a θ–2θ scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its e.s.d. were calculated from $I = \mathrm{INT} - 2(\mathrm{BGL} + \mathrm{BGR})$ and $\sigma(I) = [\mathrm{INT} + 4(\mathrm{BGL} + \mathrm{BGR})]^{0{\cdot}5}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the ω-scan range varied as $(3{\cdot}2 + 1{\cdot}25\tan\theta)$ mm and $(0{\cdot}8 + 0{\cdot}35\tan\theta)°$. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (IK)^2]^{0{\cdot}5}/2F$, where $k = 0{\cdot}02$. Of 4903 ($\pm h,+k,+l$; $h = 0$–18, $k = 0$–11, $l = 0$–21) independent measured intensities, 1992 satisfied the criterion $I \geq 2{\cdot}0\sigma(I)$, and only these were used in the solution and refinement of the structure. Computer programs used in this investigation include modified versions of the *DATAP* data reduction program (Coppens, Leiserowitz & Rabinovich, 1965), *TRACER* (Jacobson & Lawton, 1965) for cell reduction, *SHELX* (Sheldrick, 1974) for crystal-structure solution and refinement, a modified version of *ORFLS* least-squares program for blocked-diagonal refinement (Busing, Martin & Levy, 1962), *DAESD* program for distances and angles (Davis & Harris, 1970), *XANADU* molecular geometry program (Roberts & Sheldrick, 1976), and *ORTEP* thermal-ellipsoid plotting program (Johnson, 1976).

Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0·3310 (1)	0·3429 (1)	0·3330 (1)	0·044
O1	0·5427 (5)	0·4072 (8)	0·3052 (4)	0·068
O2	0·4946 (5)	0·0987 (7)	0·3741 (4)	0·062
O3	0·1517 (5)	0·410 (1)	0·2620 (5)	0·103
N1	0·3676 (5)	0·5241 (7)	0·3826 (4)	0·043
N2	0·3394 (5)	0·2806 (8)	0·4411 (4)	0·046
C1	0·3833 (7)	0·646 (1)	0·3473 (5)	0·054
C2	0·4085 (7)	0·767 (1)	0·3862 (6)	0·065
C3	0·4192 (7)	0·765 (1)	0·4649 (6)	0·062
C4	0·4025 (6)	0·643 (1)	0·5020 (5)	0·051
C5	0·3780 (5)	0·5224 (9)	0·4597 (5)	0·041
C6	0·3603 (6)	0·3839 (9)	0·4938 (5)	0·043
C7	0·3674 (6)	0·360 (1)	0·5708 (5)	0·055
C8	0·3543 (7)	0·221 (1)	0·5964 (6)	0·062
C9	0·3357 (7)	0·117 (1)	0·5440 (6)	0·058
C10	0·3290 (6)	0·148 (1)	0·4675 (5)	0·054
C11	0·4799 (6)	0·326 (1)	0·2947 (5)	0·051
C12	0·3983 (6)	0·3143 (9)	0·2414 (5)	0·046
C13	0·3729 (6)	0·1833 (9)	0·2740 (5)	0·047
C14	0·4577 (6)	0·181 (1)	0·3289 (5)	0·050
C15	0·2182 (7)	0·378 (1)	0·2909 (5)	0·060
C16	0·3248 (6)	0·0568 (9)	0·2401 (5)	0·047
C17	0·3696 (8)	−0·032 (1)	0·1959 (7)	0·072
C18	0·329 (1)	−0·149 (1)	0·1621 (6)	0·094
C19	0·242 (1)	−0·182 (1)	0·1743 (7)	0·098
C20	0·1992 (9)	−0·096 (1)	0·2175 (7)	0·088
C21	0·2394 (7)	0·022 (1)	0·2509 (6)	0·060
C22	0·3748 (7)	0·3795 (9)	0·1665 (5)	0·052
C23	0·3007 (7)	0·339 (1)	0·1178 (5)	0·069
C24	0·2839 (9)	0·396 (2)	0·0456 (6)	0·093
C25	0·340 (1)	0·500 (2)	0·0207 (7)	0·095
C26	0·412 (1)	0·541 (1)	0·0689 (7)	0·099
C27	0·4298 (8)	0·483 (1)	0·1408 (6)	0·073
C28	0·025 (2)	0·377 (3)	0·059 (2)	0·234
C29	−0·046 (2)	0·393 (4)	−0·011 (3)	0·261
C30	0·060 (2)	0·520 (9)	0·069 (3)	0·403

The structure was solved by the heavy-atom method. A difference Fourier synthesis calculated with all the non-H atoms showed evidence of a solvent molecule crystallized about a centre of symmetry. Disorder prevented unequivocal characterization of the molecule, although a six-membered ring could be clearly identified. Since the compound was recrystallized from toluene, a disordered toluene molecule is the most likely candidate, and this was modelled by three C atoms (C28–C30), which were also included in the refinement. Refinement was by blocked least-squares methods, where the function minimized was $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F)$ and $\Delta F = |F_o| - |F_c|$. The positions of the H atoms were calculated [$d(\mathrm{C{-}H}) = 0{\cdot}95$ Å] and included in the refinement with fixed isotropic thermal parameters ($U_{\mathrm{H}} = 0{\cdot}05$ Å^2). Refinement converged at $R = 0{\cdot}056$ ($wR = 0{\cdot}066$) for 325 variables and 1992 reflections and $S = 0{\cdot}94$, indicating a slight overestimation of the error of an observation of unit weight. [Refinement of the structure without the solvent molecule gave $R = 0{\cdot}108$ ($wR = 0{\cdot}167$).] In the final refinement cycle the max. shift to e.s.d. ratio was 0·05 (0·4 for the solvent). A correction for the effects of anomalous dispersion for Ni (f' 0·285, f'' 1·113) and O (f' 0·008, f'' 0·006) was included in the structure-factor calculations. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of $\pm 0{\cdot}33\ \mathrm{e\,Å^{-3}}$ were observed (1·6 Å from C28). Final atomic coordinates and selected interatomic distances and angles are given in Tables 1 and 2.* Fig. 1 shows the molecular structure.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *and torsion angles* (°), *with e.s.d.'s in parentheses*

Ni–N1	1·980 (7)	Ni–N2	1·988 (7)
Ni···C11	2·450 (9)	Ni–C12	2·035 (9)
Ni–C13	1·987 (9)	Ni···C14	2·475 (9)
Ni–C15	1·82 (1)	O1–C11	1·22 (1)
O2–C14	1·21 (1)	O3–C15	1·12 (1)
N1–C1	1·35 (1)	N1–C5	1·35 (1)
N2–C6	1·36 (1)	N2–C10	1·36 (1)
C1–C2	1·37 (1)	C2–C3	1·38 (2)
C3–C4	1·37 (1)	C4–C5	1·39 (1)
C5–C6	1·48 (1)	C6–C7	1·37 (1)
C7–C8	1·41 (2)	C8–C9	1·36 (1)
C9–C10	1·38 (1)	C11–C12	1·47 (1)
C11–C14	1·56 (1)	C12–C13	1·44 (1)
C12–C22	1·47 (1)	C13–C14	1·52 (1)
C13–C16	1·49 (1)	C16–C17	1·38 (1)
C16–C21	1·38 (1)	C17–C18	1·38 (2)
C18–C19	1·40 (2)	C19–C20	1·34 (2)
C20–C21	1·38 (2)	C22–C23	1·39 (1)
C22–C27	1·40 (1)	C23–C24	1·38 (2)
C24–C25	1·41 (2)	C25–C26	1·36 (2)
C26–C27	1·38 (2)	C28–C29	1·54 (6)
C28–C30	1·46 (7)	C29–C30	1·32 (7)
C15–Ni–C13	105·9 (4)	C15–Ni–C12	104·0 (4)
C15–Ni–C11	139·4 (4)	C15–Ni–N2	113·3 (4)
C15–Ni–N1	102·8 (4)	C13–Ni–N2	106·8 (3)
C13–Ni–N1	143·4 (3)	C12–Ni–N2	138·0 (3)
C12–Ni–N1	109·0 (3)	C11–Ni–N2	106·9 (3)
C11–Ni–N1	87·6 (3)	N2–Ni–N1	81·5 (3)
C5–N1–C1	118·2 (7)	C5–N1–Ni	115·3 (5)
C1–N1–Ni	126·6 (6)	C10–N2–C6	117·4 (7)
C10–N2–Ni	127·5 (6)	C6–N2–Ni	115·1 (6)
C2–C1–N1	122·8 (9)	C3–C2–C1	119·1 (9)
C4–C3–C2	118·9 (9)	C5–C4–C3	119·5 (9)
C6–C5–C4	124·0 (8)	C6–C5–N1	114·5 (7)
C4–C5–N1	121·5 (8)	C7–C6–C5	123·7 (8)
C7–C6–N2	122·7 (8)	C5–C6–N2	113·6 (7)
C8–C7–C6	118·5 (9)	C9–C8–C7	119·1 (9)
C10–C9–C8	119·5 (9)	C9–C10–N2	122·9 (9)
C14–C11–C12	88·6 (7)	C14–C11–O1	134·5 (8)
C12–C11–O1	136·7 (9)	C22–C12–C13	132·5 (8)
C22–C12–C11	129·9 (8)	C13–C12–C11	93·2 (7)
C16–C13–C14	125·6 (8)	C16–C13–C12	132·4 (7)
C14–C13–C12	91·1 (7)	C13–C14–C11	87·0 (7)
C13–C14–O2	136·4 (8)	C11–C14–O2	136·4 (8)
O3–C15–Ni	174 (1)	C21–C16–C17	118·4 (9)
C21–C16–C13	124·1 (8)	C17–C16–C13	117·6 (9)
C18–C17–C16	121 (1)	C19–C18–C17	120 (1)
C20–C19–C18	119 (1)	C21–C20–C19	121 (1)
C20–C21–C16	121 (1)	C27–C22–C23	117·9 (9)
C27–C22–C12	119·8 (9)	C23–C22–C12	122·2 (8)
C24–C23–C22	120 (1)	C25–C24–C23	121 (1)
C26–C25–C24	118 (1)	C27–C26–C25	121 (1)
C26–C27–C22	121 (1)	C30–C28–C29	103 (3)
C30–C29–C28	135 (3)	C29–C30–C28	118 (4)
C13–C12–C22–C23	19 (1)	C12–C13–C16–C17	73 (1)
Ni–C13–C12–C11	86 (1)	Ni–C12–C13–C14	−88 (1)
C22–C12–C13–C16	11 (1)	O1–C11–C14–O2	−3 (1)

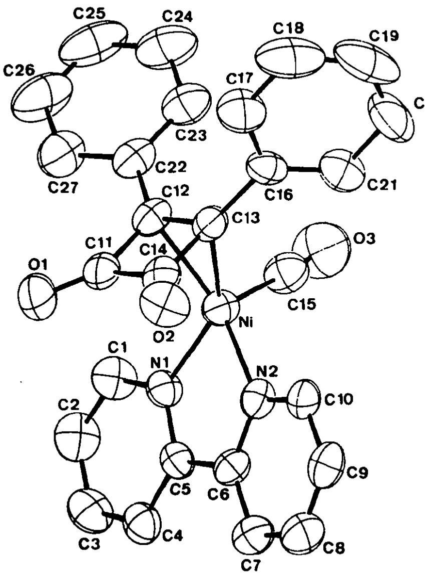

Fig. 1. The molecular structure of the title compound, showing the arbitrary numbering scheme.

Discussion. The results of the X-ray analysis reveal that the cyclobutenedione ligand is bonded to the Ni atom *via* its olefinic bond, C12=C13. The Ni—C distances to the two C atoms at 2·035 (9) (C12) and 1·987 (9) Å (C13) are significantly shorter than those to the other two C atoms in the cyclobutenedione ring [C11 2·450 (9), C14 2·475 (9) Å]. Some weak interaction between the Ni atom and C11—C14 cannot, however, be ruled out since the plane of the four-membered ring makes an angle of only 87° to that defined by Ni, C12 and C13. The comparable angle involving the Pt atom in (1-methyl-2-phenylcyclobutenedione)bis(triphenylphosphine)platinum(0) is 98° (Russell & Tucker, 1976), which would suggest that there is more interaction between the metal atom and the dione C atoms in the case of Ni. This appears somewhat surprising since the Ni atom already has its full contingent of electrons. Trigonal-planar-coordinated Pt complexes are, however, known to be particularly stable and, besides, any π-acceptor ability exhibited by the Pt atom suitable for interaction with the dione is expected to be perpendicular to the coordination plane of the metal (Hoffmann & Rösch, 1974). This may perhaps explain why the olefinic bond is twisted by 17° out of the coordination plane of the Pt atom and is not coplanar, as in other tris(ligand) complexes of the d^{10} transition metals such as tris(ethylene)nickel (Howard, Mason & Spencer, 1983).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44642 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

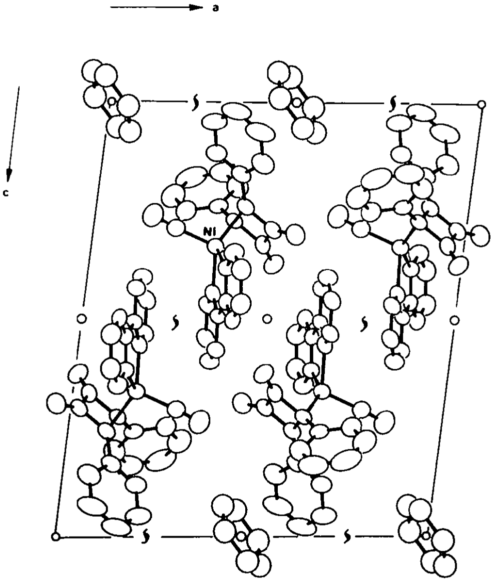

Fig. 2. The packing of the title compound in the unit cell, viewed down **b** looking towards the origin. The six C atoms defining the disordered toluene molecule are shown as circles with a radius of 0·3 Å.

The C12=C13 bond is 1·44 (1) Å and is shorter than that found in the Pt complex [1·53 (3) Å], but longer than that in phenylcyclobutenedione (Wong, Marsh & Schomaker, 1964), which itself has an olefinic bond length of 1·358 (6) Å. Bond lengths within the cyclobutenedione ring are otherwise comparable with those in the Pt compound. Bond distances and angles in the remainder of the molecule are as expected. The phenyl rings attached to C12 and C13 are bent out of the plane of the four-membered ring away from the Ni atom (C16–C21 23·2; C22–C27 19·2°) and are twisted by different amounts about the bonds linking them to the four-membered ring (Table 2). One, defined by the atoms C16–C21, is almost coplanar with a plane passing through Ni, C11 and C13 whereas the other lies almost coplanar (22°) with the four-membered ring. This asymmetry is also reflected in the bond lengths of the Ni atom to the C atoms of the cyclobutene ring and may be a result of crystal packing forces. There are, however, no intermolecular contacts between non-H atoms less than 3·2 Å. Fig. 2 shows the packing of the molecules in the unit cell.

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Structure of the Orange Modification of Diisobutylammonium Tetrachlorocuprate(II)

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Abstract. $[NH_2(C_4H_9)_2]_2[CuCl_4]$, $M_r = 465\cdot92$, tetragonal, $I\bar{4}$, $a = 16\cdot731\,(5)$, $c = 9\cdot095\,(4)$ Å, $V = 2545\cdot9$ Å^3, $Z = 4$, $D_m = 1\cdot217$, $D_x = 1\cdot22$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 13\cdot1$ cm^{-1}, $F(000) = 988$, $T = 293$ K, $R = 0\cdot048$ for 919 reflections with $I > 3\sigma(I)$. The crystal structure of $[(^i\mathrm{Bu})_2NH_2]_2[CuCl_4]$ consists of two symmetrically independent $CuCl_4^{2-}$ anions in special positions and $[(^i\mathrm{Bu})_2NH_2]^+$ cations in