

Os1—N3	2.115 (9)	Fe2—O22	2.040 (8)
Os1—N4	2.124 (8)	Fe2—O34'	2.070 (7)
Os2—O3	1.732 (7)	Fe2—O46	2.159 (7)
Os2—O4	1.740 (7)	Fe2—O47	2.089 (7)
Os3—O5	1.842 (6)	Fe3—O5	1.820 (6)
Os3—O6	1.853 (6)	Fe3—O9	2.001 (8)
Os3—N13	2.130 (8)	Fe3—O32	2.090 (6)
Os3—N14	2.111 (8)	Fe3—O39	2.067 (7)
Os3—N15	2.105 (8)	Fe3—O51	2.066 (8)
Os3—N16	2.093 (9)	Fe3—O54	2.135 (7)
Os4—O7	1.850 (6)	Fe4—O6	1.797 (6)
Os4—O8	1.838 (6)	Fe4—O18	2.069 (6)
Fe1—O7	1.790 (6)	Fe4—O25	2.071 (8)
Fe1—O15	2.075 (8)	Fe4—O33	2.071 (6)
Fe1—O29	2.074 (7)	Fe4—O43	2.094 (8)
O1—Os1—O2	179.0 (3)	O6—Os3—N15	89.1 (3)
O1—Os1—N1	90.4 (3)	O6—Os3—N16	91.2 (3)
O1—Os1—N2	88.6 (3)	N13—Os3—N14	80.4 (3)
O1—Os1—N3	91.9 (3)	N13—Os3—N15	178.7 (3)
O1—Os1—N4	89.4 (3)	N13—Os3—N16	99.3 (3)
O2—Os1—N1	89.9 (4)	N14—Os3—N15	99.3 (3)
O2—Os1—N2	90.5 (3)	N14—Os3—N16	178.9 (3)
O2—Os1—N3	89.0 (3)	N15—Os3—N16	81.0 (3)
O2—Os1—N4	90.3 (3)	O7—Fe1—O15	96.1 (3)
N1—Os1—N2	80.9 (3)	O7—Fe1—O29	98.9 (3)
N1—Os1—N3	99.4 (3)	O7—Fe1—O37'	98.7 (3)
N1—Os1—N4	179.4 (3)	O7—Fe1—O55	101.3 (3)
N2—Os1—N3	179.4 (3)	O15—Fe1—O29	92.0 (3)
N2—Os1—N4	98.5 (3)	O15—Fe1—O37'	94.6 (3)
N3—Os1—N4	81.1 (3)	O15—Fe1—O55	162.6 (3)
O3—Os2—O4	177.4 (4)	O29—Fe1—O37'	160.4 (3)
O5—Os3—O6	179.0 (3)	O29—Fe1—O55	85.6 (3)
O5—Os3—N13	87.0 (3)	O37'—Fe1—O55	82.6 (3)
O5—Os3—N14	89.4 (3)	Os3—O5—Fe3	175.5 (4)
O5—Os3—N15	91.7 (3)	Os3—O6—Fe4	172.3 (5)
O5—Os3—N16	89.6 (3)	Os4—O7—Fe1	171.2 (4)
O6—Os3—N13	92.2 (3)	Os4—O8—Fe2	178.1 (4)
O6—Os3—N14	89.9 (3)		

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$.

H atoms bound to N or C were located easily in difference maps, but water H atoms were not. The former were calculated at ideal positions with isotropic displacement parameters 1.3 times those of the attached atom, while the latter were not included in the least-squares calculations.

Data collection: *SMART* (Siemens, 1997). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *LSTSQ* in *NRCVAX* (Gabe *et al.*, 1989). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *NRCVAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1073). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
 Coelho, A. L. & Malin, J. M. (1975). *Inorg. Chim. Acta*, **14**, L41–43.

- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
 Malin, J. M., Schlemper, E. O. & Murmann, R. K. (1977). *Inorg. Chem.* **16**, 615–619.
 Malin, J. M. & Taube, H. (1971). *Inorg. Chem.* **10**, 2473–2478.
 Murmann, R. K. (1977). *J. Inorg. Nucl. Chem.* **39**, 1317–1320.
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Siemens (1997). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Tricarbonyliron complexes derived from dimethyl 1,3-butadiene-2,3-dicarboxylate: formation of $[\text{Fe}(\text{CO})_3]_2$ -dimethyl 1,3-butadiene-2,3-dicarboxylate

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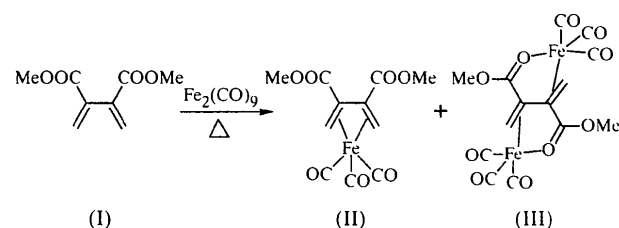
Abstract

Treatment of dimethyl 1,3-butadiene-2,3-dicarboxylate with $\text{Fe}_2(\text{CO})_9$ provided the corresponding tricarbonyl(η^4 -dimethyl 1,3-butadiene-2,3-dicarboxylato-*O*)iron, $[\text{Fe}(\text{C}_8\text{H}_{10}\text{O}_4)(\text{CO})_3]$, (II), as the main product and the novel μ -[(1,2- $\eta, \kappa\text{O}^3$:3,4- $\eta, \kappa\text{O}^2$)-dimethyl 1,3-butadiene-2,3-dicarboxylato]bis(tricarbonyliron), $[\text{Fe}_2(\text{C}_8\text{H}_{10}\text{O}_4)(\text{CO})_6]$, (III). In the crystal structure of (II), the electron-deficient butadiene complexes with one $\text{Fe}(\text{CO})_3$ group, whereas in (III), the butadiene adopts an unusual conformation and forms a complex with two $\text{Fe}(\text{CO})_3$ groups. In (III), each Fe atom possesses a trigonal bipyramidal geometry, with one olefinic bond and two carbonyl ligands occupying the basal positions, and the keto oxygen of the ester and the other carbonyl ligand occupying apical positions.

Comment

The chemistry of $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$ complexes has been the subject of intense study and it is now well recognized that these complexes can serve as valuable

synthetic intermediates (Freccero *et al.*, 1998; Gree, 1989; Iwata & Takemoto, 1996; Ripoche *et al.*, 1998; Ban *et al.*, 1998; Cox & Ley, 1998; Sammelhack *et al.*, 1983; Pearson *et al.*, 1998). However, complexes derived from certain electron-deficient butadienes, for example, dimethyl 1,3-butadiene-2,3-dicarboxylate, (I), were unknown. The diene (I) has long been speculated to serve not only as a useful precursor in organic synthesis, but also as a building block in the preparation of novel types of polymeric materials (Bailey *et al.*, 1963). Indeed, after the straightforward large-scale synthesis of (I) was reported (Tarnchompoo *et al.*, 1987), this compound has been used in the total syntheses of natural products (Mahidol *et al.*, 1989) and other macromolecules (Kotera *et al.*, 1994, 1995). We report herein the formation of two tricarbonyliron complexes formed from the reaction of (I) and Fe₂(CO)₉.



Compound (II) (Fig. 1) gave spectroscopic and analytical data consistent with common [Fe(CO)₃(η⁴-diene)] complexes. A characteristic feature of the ¹H NMR spectrum of (II) was the presence of two doublets at 0.19 and 2.18 p.p.m. (*J* = 2.56 Hz), respectively assigned to the highly shielded *endo* and the less shielded *exo* protons at C1 (and the equivalent C4). It was apparent from the ¹H NMR spectra that the effect of the Fe(CO)₃ moieties in (III) was less pronounced than

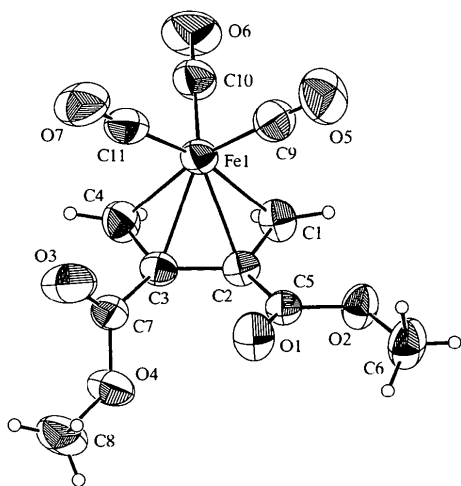


Fig. 1. The molecular structure of (II) showing 50% probability displacement ellipsoids.

that of (II) where the corresponding protons at C1 and C4 resonated as doublets at 2.38 and 2.92 p.p.m. (*J* = 3.76 Hz), respectively.

The crystallographic results of (III) (Fig. 2) reveal that the electron-deficient butadiene acts as a tetradentate ligand to form a complex with two units of Fe(CO)₃. Thus far, only a few examples of Fe–ene–one complexes have been elucidated (Alt *et al.*, 1993; de Cian *et al.*, 1980) and (III) can be viewed as a dimeric structure of Fe–ene–one in a single molecule. Compound (III) is formed by cross-complexation of the Fe1 atom to the olefinic C1–C2 atoms and the carbonyl O3 of the ester moiety. The Fe2 atom coordinates to the C3–C4 atoms and the carbonyl O1 atom in a similar manner. In so doing, the butadienyl ligand has adopted a *transoid* geometry and is no longer fully conjugated because a twisted conformation of C1–C2–C3–C4 [dihedral angle –103.9(4)°] is essential to accommodate the complexation of both Fe(CO)₃ groups. The C2–C3 bond distance in (III) of 1.501(4) Å is significantly longer than the corresponding bond of 1.424(4) Å in (II) or in other known η⁴-butadiene tricarbonyliron complexes (Cotton & Troup, 1974; Alcock *et al.*, 1988; Nakanishi *et al.*, 1998; Martina *et al.*, 1982; Mills & Robinson, 1963).

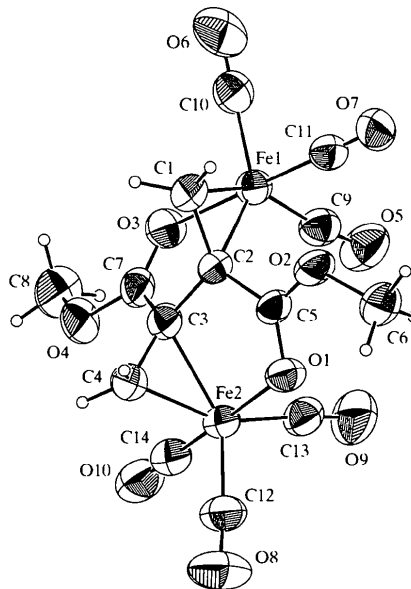


Fig. 2. The molecular structure of (III) showing 50% probability displacement ellipsoids.

Compound (III) has a chemical C₂ symmetry at the middle of the C2–C3 bond. Each metal centre possesses a trigonal bipyramidal geometry, with one olefinic bond and two of the carbonyl ligands occupying the basal positions, and the keto oxygen of the ester and

the other carbonyl ligands occupying apical positions. The two Fe—O distances are quite similar, *ca* 2.03 Å, while the Fe1—C7 and Fe2—C5 distances are well outside the bonding range (2.79 Å). The η^1 (O) coordination of the keto group to the electron-deficient tricarbonyl-iron weakens the C=O double bond quite significantly [1732 cm⁻¹ in (II) *versus* 1575 cm⁻¹ in (III)] due to the absence of the *M* → *L* π -back bonding (Gambarotta *et al.*, 1981). Evidently, the C=O bond (C5—O1) distance of 1.237 (5) Å is longer than the typical carbonyl bond lengths of 1.186 (4) and 1.198 (4) Å found in (II). In addition, the η^1 -coordination of the keto oxygen to metal, having a *trans* effect to the opposite carbonyl group, contributes to a stronger *M*—CO back bonding, and hence shortens the Fe—CO distances to 1.745 (4) and 1.760 (5) Å compared with a range of 1.812 (4)–1.832 (4) Å for other similar bonds.

Experimental

A mixture of dimethyl 1,3-butadiene-2,3-dicarboxylate [(I); 54.5 mg, 32 mmol] and Fe₂(CO)₉ (233.1 mg, 64 mmol) in dioxane (3.0 ml) was heated under argon at 323 K for 1 h. After the reaction mixture had cooled to room temperature, a dark-brown precipitate was filtered off. The filtrate was then evaporated under vacuum. The crude product, dissolved in CH₂Cl₂, was adsorbed onto a silica-gel column and eluted with hexane–ethyl acetate (95:5) to provide complexes (II) (46.2 mg, 62% yield) and (III) (6.6 mg, 6% yield). Crystals of both complexes suitable for X-ray diffraction studies were prepared by slow evaporation from a CH₂Cl₂/hexane solution at 277 K.

Compound (II)

Crystal data

[Fe(C₈H₁₀O₄)(CO)₃]

M_r = 310.04

Monoclinic

*P*2₁/*c*

a = 6.7367 (5) Å

b = 13.6547 (5) Å

c = 14.2727 (4) Å

β = 93.392 (5)°

V = 1310.6 (2) Å³

Z = 4

D_x = 1.571 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

θ – 2θ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

T_{min} = 0.712, *T_{max}* = 0.791

5967 measured reflections

2567 independent reflections

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 2.0–25.9°

μ = 1.18 mm⁻¹

T = 295 (2) K

Prism

0.50 × 0.25 × 0.20 mm

Yellow

2091 reflections with
*F*² > 3 σ (*F*²)

R_{int} = 0.028

θ_{\max} = 25.9°

h = 0 → 8

k = –16 → 0

l = –17 → 17

3 standard reflections

frequency: 60 min

intensity decay: 10.8%

Refinement

Refinement on *F*²

R(*F*) = 0.039

wR(*F*²) = 0.123

S = 0.862

2567 reflections

172 parameters

H atoms constrained

w = 1/[σ^2 (*F_o*²) + (0.0772*P*)²
+ 2.0217*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$\Delta\rho_{\max}$ = 0.34 e Å⁻³

$\Delta\rho_{\min}$ = –0.66 e Å⁻³

Extinction correction: none

Scattering factors from
Waasmaier & Kirfel
(1995)

Table 1. Selected geometric parameters (Å, °) for (II)

Fe1—C11	1.805 (4)	O1—C5	1.198 (4)
Fe1—C9	1.791 (4)	C4—C3	1.423 (4)
Fe1—C1	2.103 (3)	C5—C2	1.489 (4)
Fe1—C2	2.055 (3)	O3—C7	1.186 (4)
Fe1—C3	2.054 (3)	C1—C2	1.419 (4)
Fe1—C4	2.107 (4)	C2—C3	1.424 (4)
Fe1—C10	1.785 (4)	C3—C7	1.494 (4)
C1—C2—C3—C4	–0.2 (3)		

Compound (III)

Crystal data

[Fe₂(C₈H₁₀O₄)(CO)₆]

M_r = 449.92

Triclinic

P $\bar{1}$

a = 7.6839 (4) Å

b = 8.7128 (9) Å

c = 14.049 (1) Å

α = 105.614 (8)°

β = 97.418 (5)°

γ = 102.040 (6)°

V = 868.6 (3) Å³

Z = 2

D_x = 1.720 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

θ – 2θ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

T_{min} = 0.632, *T_{max}* = 0.709

6487 measured reflections

3044 independent reflections

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 2.0–24.9°

μ = 1.72 mm⁻¹

T = 295 (2) K

Prism

0.30 × 0.20 × 0.20 mm

Dark red

2583 reflections with
*F*² > 3 σ (*F*²)

R_{int} = 0.017

θ_{\max} = 24.9°

h = –9 → 9

k = –10 → 10

l = –16 → 16

3 standard reflections

frequency: 60 min

intensity decay: 1.6%

Refinement

Refinement on *F*²

R(*F*) = 0.037

wR(*F*²) = 0.113

S = 0.883

3044 reflections

235 parameters

H atoms constrained

w = 1/[σ^2 (*F_o*²) + (0.0808*P*)²
+ 0.9113*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

$\Delta\rho_{\max}$ = 0.31 e Å⁻³

$\Delta\rho_{\min}$ = –0.67 e Å⁻³

Extinction correction: none

Scattering factors from
Waasmaier & Kirfel
(1995)

Table 2. Selected geometric parameters (Å, °) for (III)

Fe1—O3	2.030 (3)	Fe2—C13	1.812 (4)
Fe1—C1	2.042 (4)	Fe2—C14	1.745 (4)
Fe1—C2	2.071 (3)	O1—C5	1.237 (5)
Fe1—C9	1.832 (4)	O3—C7	1.246 (5)
Fe1—C10	1.817 (5)	C1—C2	1.431 (5)
Fe1—C11	1.760 (5)	C2—C3	1.502 (4)
Fe2—O1	2.036 (3)	C2—C5	1.447 (5)
Fe2—C3	2.067 (4)	C3—C4	1.429 (5)
Fe2—C4	2.034 (4)	C3—C7	1.446 (5)
Fe2—C12	1.815 (5)		
O3—Fe1—C1	88.6 (2)	C9—Fe1—C11	90.4 (2)
O3—Fe1—C2	80.7 (1)	C10—Fe1—C11	90.6 (2)
O3—Fe1—C9	91.0 (2)	O1—Fe2—C14	175.1 (2)
O3—Fe1—C10	90.3 (2)	Fe2—O1—C5	114.8 (2)
O3—Fe1—C11	178.1 (2)	Fe1—O3—C7	114.7 (3)
C9—Fe1—C10	105.4 (2)		
C1—C2—C5—O1	168.6 (5)	C4—C3—C7—O3	170.6 (6)
C1—C2—C3—C4	-103.9 (4)		

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *maxUs* (Mackay *et al.*, 1999); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *maxUs*; software used to prepare material for publication: *maxUs*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1020). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W., Cout, D. H. G., Henderson, C. M. & Thomas, S. E. (1988). *J. Chem. Soc. Chem. Commun.* pp. 746–747.
- Alt, C., Griffiths, S. L., Marcos, C. F., Salter, M. M., Slawin, A. M. Z., Thomas, S. E. & Williams, D. J. (1993). *J. Chem. Soc. Chem. Commun.* pp. 201–203.
- Bailey, W. J., Hudson, R. L. & Yates, E. T. (1963). *J. Org. Chem.* **28**, 828–831.
- Ban, S. H., Hayashi, Y. & Narasaka, K. (1998). *Chem. Lett.* pp. 393–396.
- Cian, A. de, Weiss, R., Haudegond, J.-P., Chauvin, Y. & Commereuc, D. (1980). *J. Organomet. Chem.* **187**, 73.
- Cotton, F. A. & Troup, J. M. (1974). *J. Organomet. Chem.* **77**, 369–379.
- Cox, L. R. & Ley, S. V. (1998). *Chem. Soc. Rev.* **27**, 301–314.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Freccero, M., Gandolfi, R. & Sarzi-Amade, M. (1998). *Heterocycles*, **49**, 415–426.
- Gambarotta, S., Pasquali, M., Floriani, C. & Chiesi-Villa, A. (1981). *Inorg. Chem.* **20**, 1173–1178.
- Gree, R. (1989). *Synthesis*, pp. 341–355.
- Iwata, C. & Takemoto, Y. (1996). *Chem. Commun.* pp. 2497–2504.
- Kotera, M., Lehn, J.-M. & Vigneron, J.-P. (1994). *J. Chem. Soc. Chem. Commun.* pp. 197–199.
- Kotera, M., Lehn, J.-M. & Vigneron, J.-P. (1995). *Tetrahedron*, **51**, 1953–1972.

- Mackay, S., Edwards, C., Henderson, A., Gilmore, C., Stewart, N., Shankland, K. & Donald, A. (1999). *maxUs: Comprehensive Crystallographic Program*. University of Glasgow, Scotland.
- Mahidol, C., Tarnchompoo, B., Thebtaranonth, C. & Thebtaranonth, Y. (1989). *Tetrahedron Lett.* **30**, 3861–3864.
- Martina, D., Brion, F. & de Cian, A. (1982). *Tetrahedron Lett.* **23**, 857–868.
- Mills, O. S. & Robinson, G. (1963). *Acta Cryst.* **16**, 758–761.
- Nakanishi, S., Nakanishi, J.-I. & Takata, T. (1998). *Synth. Commun.* **28**, 1967–1979.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pearson, A. J., Alimardanov, A., Pinkerton, A. A. & Parrish, D. A. (1998). *J. Org. Chem.* **63**, 6610–6618.
- Ripoche, I., Canet, J.-L., Aboab, B., Gelas, J. & Troin, Y. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 3485–3492.
- Sammelhack, M. F., Herndon, J. W. & Springer, J. P. (1983). *J. Am. Chem. Soc.* **105**, 2497–2499.
- Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Tarnchompoo, B., Thebtaranonth, C. & Thebtaranonth, Y. (1987). *Tetrahedron Lett.* **28**, 6671–6674.
- Waasmaier, D. & Kirfel, A. (1995). *Acta Cryst.* **A51**, 416–431.

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(Carbonato-*O,O'*)bis(propane-1,3-diyl-diamine-*N,N'*)cobalt(III) chloride monohydrate

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Abstract

In the cation of the title compound, [Co(C₃H₁₀N₂)₂-(CO₃)Cl·H₂O] or [Co(pren)₂(CO₃)Cl·H₂O], where pren is trimethylenediamine (C₃H₁₀N₂), the metal atom is chelated by two pren ligands and a carbonate anion in a distorted octahedral geometry, with Co—N bond lengths in the range 1.922 (3)–1.945 (3) Å and Co—O bond lengths of 1.885 (3) and 1.901 (3) Å.

Comment

The fixation of atmospheric CO₂ by metal complexes is of special interest in environmental protection, because the fundamental understanding and application of the reaction may lead to some practical means to reduce the level of CO₂ present in the air. The development of an effective chemical method for CO₂ fixation is the