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Preparation and characterization of chromium, molybdenum and tungsten compounds containing amino acid ester derivatized diimine ligands. Crystal structure of $Mo(CO)_4$(pyca-β-ala-OEt)

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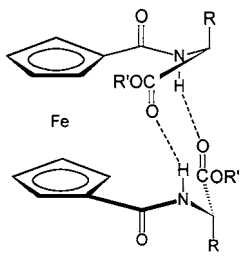
Abstract

The title compounds were prepared by heating solutions of ester-protected amino acids (H-β-Ala-OEt, H-L-Ala-OEt, H-L-Val-OMe, H-L-Asp(OMe)-OMe, GABA-OMe) and pyridine-2-carboxaldehyde in the presence of $M(CO)_4(pip)_2$ (M = Mo,W) or $[NEt_4][Cr(CO)_5I]$. The resulting novel complexes, $M(CO)_4$(pyca-xxx-OR) (pyca = pyridinecarbaldehyde imine), contain an η^2-*N*,*N*′-diimine ligand and were characterized by ^{1}H- and ^{13}C-NMR, IR and UV–vis measurements. The lone band in the visible portion of the electronic spectrum is assigned to a MLCT transition and exhibits solvatochromism. The crystal structure of $Mo(CO)_4$(pyca-β-ala-OEt) (**1b**), was determined and confirms the presence of the bidentate α-diimine ligand. The metal lies in a pseudo C_s symmetry environment. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diimine; Chromium; Molybdenum; Tungsten; Amino acid; Crystal structure

1. Introduction

Transition metal ions readily incorporate amino acids as ligands [1,2]. Researchers have used this capability to model the structure and mechanistic function of biological proteins as a tool to create or cleave peptides, and as a biological marker with characteristic physical and spectroscopic properties. Of recent interest are complexes with amino acids incorporated in organometallic compounds [3]. This is becoming a fertile field of study since organometallic compounds offer unique binding environments. Commonly reported means of incorporating amino acids or peptides in organometallic compounds include π-bonding the aryl group of an amino acid to the metal center [4–7], chelating both ends of the amino acid to the metal [8–13], or covalently attaching the biological group to a cyclopentadienyl ring [14–21]. Recent work in our laboratory [22] used amino acids covalently attached to cyclopentadienyl rings to model a β-sheet. We demonstrated that L-valine and L-phenylalanine bis(amino acid) derivatives of 1,1′-ferrocenedicarboxylic acid adopt an ordered, intramolecularly hydrogen-bonded conformation in $CHCl_3$ (see below).



Derivatized amino acids have also been utilized as ligands. For example, Beck and co-workers have prepared diimine ligands from condensation of the amine of an amino acid with an aldehyde generating C,N [23,24] and N,O bidentate ligands [25,26] and N donor ligands [27].

We became interested in preparing novel ligands that would include amino acids in the coordination sphere of an organometallic complex. We were looking for a

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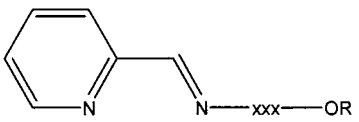
ligand that could be easily prepared, would strongly bind to organometallic centers, and would have one end of the amino acid unbound and available for potential further reaction. We targeted an α-diimine ligand system given the complexing ability of this class of ligands with most transition metals. In this paper, we report the preparation and characterization of Group 6 carbonyl complexes containing a new amino acid conjugate diimine ligand (below) based on pyridinecarbaldehyde imine (pyca).



All compounds were successfully characterized. Electronic spectra showed that the compounds exhibit solvatochromism consistent with α-diimine complexes. The molecular structure of $Mo(CO)_4$(pyca-β-ala-OEt) (**1b**) was determined to confirm the presence of the bidentate α-diimine ligand.

2. Results and discussion

2.1. Synthesis

Heating the appropriate amino acid ester as the hydrochloride salt with $M(CO)_4(pip)_2$ (M = Mo, W) or $[NEt_4][Cr(CO)_5I]$, pyridine-2-carboxaldehyde and NEt_3 in 1-propanol produced amino acid conjugate complexes, $M(CO)_4$(pyca-*N*-xxx-OR) (**1**–**6**). A general synthetic scheme for their preparation is shown in Fig. 1 and the numbering scheme utilized is summarized in Table 1. Shortly after heating began for the Cr and Mo complexes, the 1-propanol solution rapidly darkened, resulting in a deep purple or reddish–purple solution. The solution was heated to reflux to ensure complete reaction. The reactions involving tungsten compounds did not color noticeably until the reaction solution neared the reflux temperature. Tungsten compounds were refluxed for 30 min to ensure complete reaction. Attempts to prepare these compounds from the parent hexacarbonyls were unsuccessful. Piperidine [28,29] or iodo [30] substituted derivatives are often used to produce Group 6 tetracarbonyl derivatives when higher temperature reactions are not wanted.

Following washings to remove salt by-products and unreacted amine and amino acid, the compounds were recrystallized from CH_2Cl_2–hexane mixtures. Crystalline solids resulted—except for the GABA-OMe derivative (**5a**) which produced an oil—in yields from 35 to 90%. The oily nature of **5a** is likely due to the long flexible $(CH_2)_3$ chain in GABA. The compounds are air stable as solids but slowly decompose in solution. The chromium alanine derivative, **2c**, could not be prepared and purified despite the fact that **2a**–**b** were prepared uneventfully. It was not clear why this derivative could not be prepared.

A tungsten β-alanine complex (**6a**), with pyridine-2-methyl ketone replacing pyridine-2-carboxaldehyde as a reagent, was prepared for comparison purposes. The synthesis proceeded similarly to the pyca derivatives although it took considerably longer for the solution to become deeply colored and for the reaction to reach completion.

Satisfactory elemental analysis results were obtained for all metal complexes reported.

2.2. Structure of $Mo(CO)_4$(pyca-β-ala-OEt) (1b)

The compound crystallizes with two unique structures in each unit cell. The structural data concerning orientation and separation of atoms around the central

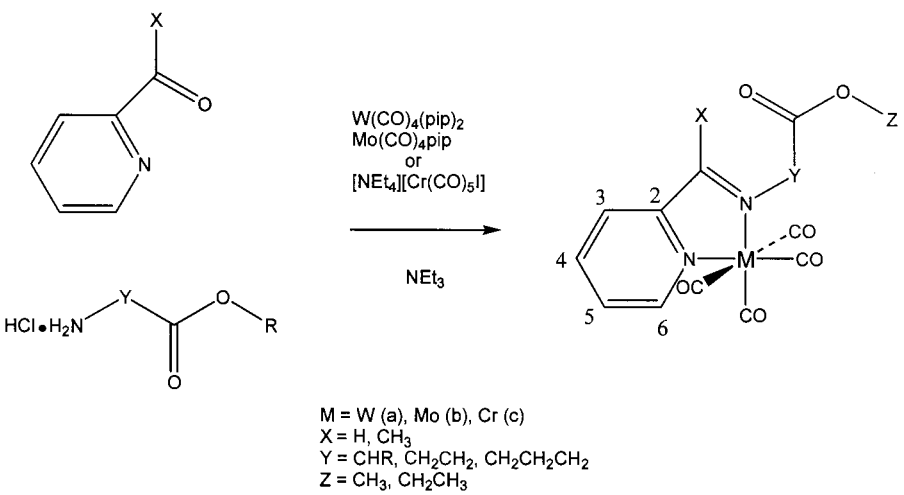


Fig. 1. General structure and labeling scheme for NMR spectral identification.

Table 1
Numbering scheme for compounds prepared

Compound	Metal [a]	Amino acid or amine	X	Y	Z
1	a, b, c	H-β-Ala-OEt	H	$-CH_2CH_2-$	Et
2	a, b	H-L-Ala-OEt	H	$-CH(CH_3)-$	Et
3	a, b, c	H-L-Val-OMe	H	$-CH(i\text{-}Pr)-$	Me
4	a, b, c	H-L-Asp(OMe)-OMe	H	$-CH(CH_2COOCH_3)-$	Me
5	a	$H_2N-(CH_2)_3-OMe$ [b]	H	$-CH_2CH_2CH_2-$	Me
6	a	H-β-Ala-OEt	Me	$-CH_2CH_2-$	Et
7	a	H_2NEt	H	$-CH_2CH_3$	–
8	–	H-β-Ala-OEt	H	$-CH_2CH_2-$	Et

[a] a = W, b = Mo, c = Cr.
[b] GABA is γ-aminobutyric acid.

metal are similar for each structure. Data are presented for only one structure; data for the other structure can be found in the Supplemental Tables. The structure of **1b** is illustrated in Fig. 2. Crystal data are given in Table 2, relevant bond lengths and angles in Table 3, and atom coordinates in Table 4.

The compound presents a slightly distorted octahedral coordination environment around Mo. Its structural features closely resemble those of several $Mo(CO)_4$(diimine) compounds reported previously [31–35], including the pyca derivative $Mo(CO)_4$[pyca-$CH(CH_3)$(Ph)] [36]. The distortion is caused by the 72.58(9)° bite angle of the bidentate pyca ligand. The two mutually *trans* carbonyls bend away from the pyca ligand as demonstrated by the C10–Mo–C7 bond angle of 167.7(1)°. The two Mo–N bond lengths are Mo–N1 = 2.237(2) Å, Mo–N2 = 2.243(2) Å. The pyridine and imine portion of the pyca ligand is planar as expected by the demands of conjugation and the associated geometric constraints of metal to ligand backbonding. The sum of the *cis* angles involving Mo and the plane defined by N1, N2, C8 and C9 is 360.1(4)°. The C5–C6 and C6–N1 bond lengths of 1.453(4) and 1.285(4) Å, respectively, support the claim of conjugation. The amino acid fragment is oriented to maximize packing in the crystal. In solution rotation would move the fragment through a position where the carbon backbone of the achiral β-alanine conjugate lies in the plane of the diimine ligand giving rise to the molecular plane (C_s symmetry) apparent in the ^{13}C-NMR.

2.3. Spectroscopic characterization

IR spectra in CH_2Cl_2 show four metal carbonyl bands with the pattern and energies expected for a *cis*-substituted tetracarbonyl complex [37]. In addition a weaker carbonyl band due to the ester carbonyl is observed around 1735 cm^{-1}.^{13}C resonances (Table 5) of the metal carbonyls in **1** and **5**–**7** show three resonances with the upfield resonance having greater intensity. This suggests these molecules possess a plane of symmetry (point group C_s). The upfield resonance is assigned to the two mutually *trans* carbonyls (CO_{trans}). The other two peaks are assigned to the two *cis* carbonyls (CO_{cis}, each is *trans* to an imine nitrogen). These carbonyls each occupy unique environments accounting for the separate peaks displayed. Compounds **2**–**4** show four equal intensity resonances, with the two upfield very close together. This is a consequence of the chirality of L-alanine, L-valine and L-phenyl aspartic acid. The loss of the mirror plane results in (slightly) different resonances for the mutually *trans* carbonyls. The ordering of related carbonyl carbon resonances is Cr > Mo > W. The pyridine carbon resonances occur in expected regions and the imine carbon displays a resonance at 163–170.1 ppm. Other resonances were in accord with expectations. ^1H-NMR spectra were distinguished (Table 6) by a single peak between 8.7 and 9.0 ppm due to the imine hydrogen. Maintenance of the unreacted ester of the diimine ligand was confirmed by appropriate resonances for the molecule associated with Y and Z in Fig. 1.

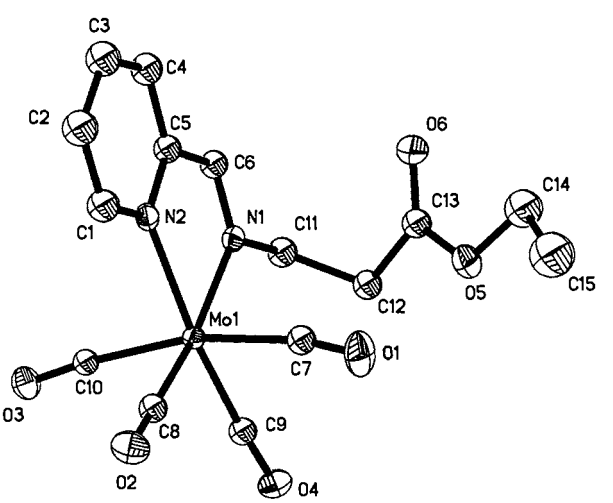


Fig. 2. Molecular structure (ORTEP drawing) for $Mo(CO)_4$(pyca-β-ala-OEt) (**1b**).

Table 2
Crystallographic data for **1b**

Empirical formula	$C_{15}H_{14}N_2O_6Mo$
Formula weight	414.22
Crystal system	Monoclinic
Space group	$P2/n$
a (Å)	19.8825(8)
b (Å)	9.1249(4)
c (Å)	20.6188(8)
β (°)	117.0100(10)
V (Å^3)	3332.8(2)
Z	8
$F(000)$	1664
T (K)	120(1)
λ (Å)	0.71073
$\rho_{calc.}$ (g cm^{-3})	1.651
Absorption coefficient (mm^{-1})	0.820
θ range for data collection (°)	1.18–28.33
GOF	1.101
R [a]	0.0379
R_w [b]	0.0867

[a] $R = \Sigma[|F_o|-|F_c|/\Sigma|F_o|]$.
[b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ $w = 1/[\delta^2(F_o)+g(F_c)]$ $g = 0.002$.

2.4. Electronic spectroscopy

The compounds form deeply colored red to royal blue solutions in non-polar solvents while they are pink or orange in polar solvents. Visible spectroscopy shows a single intense band for these complexes that falls between 490 and 590 nm (Table 7). This band is assigned to a metal-to-ligand charge-transfer (MLCT) transition based on three points: (1) neither the free ligand (colorless) or the metal precursors (yellow) show a similar band. (2) The band is more intense than expected for a LF-based band. (3) Finally, a substantial negative solvatochromism effect is observed for spectra obtained in toluene (lower energy) and methanol (higher energy), see Table 7. Similar spectral behavior has been observed for various Group 6 compounds with 2,2′-bipyridine, 1,4-diaza-1,3-butadiene and pyca ligands [38–40]. The energy shift, Δ, for each compound on changing solvent was measured and varies between 1082 and 1520 cm^{-1}. Values between 700 and 2000 cm^{-1} have been measured for Group 6 and Group 7 compounds [38,41]. Molar absorptivities between 4400 and 12 000 M^{-1} cm^{-1}, indicative of charge transfer transitions [42], were calculated for these compounds. The molar absorptivities for each compound were larger for toluene solutions than for the corresponding methanol solutions. Within series of amino acid congeners, the λ_{max} varies in the trend –Cr > W > Mo as observed for related bipyridyl-type compounds [43]. The presence of an electron-withdrawing ester group proximal to the diimine moves the transition to lower energy (compounds **2**–**4**) compared with compounds with two or more CH_2 groups separating ester and imine (**1a**–**c** and **5a**) or not containing an ester group (**7a**). The nature of the group attached to the imine carbon also has a significant effect on the electronic spectrum. When the imine hydrogen in **1a** is replaced with a more electron-releasing methyl group (**6a**), λ_{max} is lowered about 15 nm in both methanol and toluene. These findings are constituent with previous work on MLCT transitions for pyridine, bipyridine and related Group 6 compounds [44].

Table 3
Selected bond lengths (Å) and bond angles (°) for **1b**

Bond lengths (Å)			
Mo–C9	1.964(3)	Mo–C8	1.971(3)
Mo–C7	2.042(3)	Mo–C10	2.051(3)
Mo–N1	2.237(2)	Mo–N2	2.243(2)
C5–C6	1.453(4)	C6–N1	1.285(4)
Bond angles (°)			
C9–Mo–C8	93.0(1)	C9–Mo–C7	83.8(1)
C8–Mo–C7	83.9(1)	C9–Mo–C10	87.8(1)
C8–Mo–C10	87.6(1)	C7–Mo–C10	167.7(1)
C9–Mo–N1	97.1(1)	C8–Mo–N1	169.8(1)
C7–Mo–N1	95.5(1)	C10–Mo–N1	94.4(1)
C9–Mo–N2	169.7(1)	C8–Mo–N2	97.4(1)
C7–Mo–N2	97.0(1)	C10–Mo–N2	92.8(1)
N1–Mo–N2	72.58(9)		

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **1b** [a]

Atom	x	y	z	U_{eq}
Mo	5983(1)	328(1)	3396(1)	14(1)
O1	4903(2)	123(3)	1698(1)	38(1)
O2	5258(1)	−2746(3)	3347(1)	32(1)
O3	6591(1)	239(2)	5118(1)	25(1)
O4	4609(1)	2112(3)	3321(1)	32(1)
O5	5275(1)	3423(3)	1407(1)	28(1)
O6	6477(1)	4206(3)	1986(1)	36(1)
N1	6661(1)	2276(3)	3384(1)	18(1)
N2	7060(1)	−510(3)	3432(1)	20(1)
C1	7265(2)	−1924(4)	3458(2)	29(1)
C2	7927(2)	−2362(4)	3443(2)	35(1)
C3	8404(2)	−1300(4)	3402(2)	33(1)
C4	8216(2)	164(4)	3393(2)	27(1)
C5	7542(2)	523(3)	3409(2)	21(1)
C6	7300(2)	2031(3)	3391(2)	21(1)
C7	5346(2)	228(3)	2292(2)	23(1)
C8	5522(2)	−1591(3)	3381(2)	22(1)
C9	5114(2)	1413(3)	3362(2)	21(1)
C10	6414(2)	292(3)	4507(2)	18(1)
C11	6422(2)	3819(3)	3347(2)	24(1)
C12	5726(2)	4121(3)	2629(2)	22(1)
C13	5883(2)	3927(3)	1984(2)	23(1)
C14	5335(2)	3323(4)	728(2)	39(1)
C15	4740(3)	2309(6)	235(3)	55(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
^{13}C-NMR [a] for reported compounds

	CO_{cis}	CO_{trans}	C2	C3	C4	C5	C6	C=N	–C	C	OCO	Other
1a	216.7, 215.0	198.2	155.3	128.0	136.9	126.9	153.0	165.6	– [b]	35.8	171.5	61.8 (CH_2), 61.1 (CH_2), 14.2 (CH_3)
1b	223.4, 222.6	203.0	153.8	127.8	137.2	126.3	153.2	164.0	– [b]	35.1	174.5	61.1 (CH_2), 60.9 (CH_2), 14.3 (CH_3)
1c	230.2, 229.2	212.2	154.8	126.8	136.2	125.4	153.6	163.2	– [b]	35.2	171.6	61.0 (CH_2), 60.7 (CH_2), 14.3 (CH_3)
2a	217.0, 214.0	198.2, 198.1	155.2	128.4	136.7	127.1	153.1	164.3	71.6	20.0	170.0	62.7 (CH_2), 14.2 (CH_3)
2b	223.9, 221.8	203.1, 202.9	153.7	128.1	137.0	126.5	153.3	163.2	71.0	19.4	169.8	62.5 (CH_2), 14.2 (CH_3)
3a	217.2, 214.1	198.1, 198.0	155.3	128.6	136.6	127.1	153.0	164.3	82.3	32.4	170.5	53.0 (OCH_3),19.7 (CH_3), 19.4 (CH_3)
3b	224.0, 221.6	203.0, 202.8	153.7	128.3	136.9	126.6	153.3	163.5	82.3	31.6	170.0	52.8 (OCH_3),19.7 (CH_3), 19.5 (CH_3)
3c	230.8, 227.8	212.0	154.7	127.7	136.2	125.6	153.5	162.5	80.9	31.9	170.9	52.8 (OCH_3),19.6 (CH_3), 19.5 (CH_3)
4a	216.2, 213.3	197.8, 197.7	154.7	129.0	136.8	127.4	153.0	168.3	73.0	37.6	171.2, 168.2	53.6 (CH_3), 52.5 (CH_3)
4b	223.3, 221.3	202.8, 202.5	153.4	128.6	137.1	126.9	153.4	166.6	72.2	37.0	171.3, 168.2	53.4 (CH_3), 52.2 (CH_3)
4c	230.3, 227.6	212.0, 211.8	154.3	128.0	136.3	126.0	153.6	165.9	72.3	36.9	171.3, 168.5	53.3 (CH_3), 52.3 (CH_3)
5a	217.1, 215.0	198.4	155.5	127.6	136.7	126.8	153.1	163.8	65.6	– [b]	173.3	52.0, (OCH_3), 30.8 (CH_2), 27.5 (CH_2)
6a	216.4, 215.0	199.2	157.1	126.6	136.7	126.5	153.0	170.2	– [b]	36.2	171.3	55.1 (CH_2), 61.1 (CH_2), 16.4 (CH_3), 14.3 (CH_3)
7a	217.3, 215.3	198.6	155.6	127.4	136.8	126.7	153.0	162.6	61.6	18.2		
8	–	–	154.7	124.8	136.5	121.5	149.6	163.1	– [b]	35.6	171.9	60.5 (CH_2), 56.6 (CH_2), 12.6 (CH_3)

[a] Recorded in $CDCl_3$. See Fig. 1 for adopted numbering scheme.
[b] CH_2 groups could not be distinguished.

3. Experimental

3.1. Spectroscopic measurements

NMR spectra were recorded on a Bruker AC-300 spectrometer. IR spectra were recorded on a Perkin–Elmer 1750 FT-IR spectrometer, while electronic spectra were obtained from a Hitachi U-2000 spectrometer. Elemental analyses were performed by Atlantic Microlab of Norcross, GA 30091.

3.2. Materials

Starting materials for syntheses were obtained from commercial sources and used without further purification. All solvents were degassed prior to use. All preparations were performed under a nitrogen atmosphere. $M(CO)_4(pip)$ (M = Mo, W; pip = piperidine) [28] and $[NEt_4][Cr(CO)_5I]$ [30] were prepared using literature procedures.

3.3. Synthesis of *1a–4a*

In a typical procedure the amino acid, H-xxx-OR·HCl (1.07 mmol), pyridine-2-carboxaldehyde (0.115 g, 1.07 mmol) and NEt_3 (0.108 g, 1.07 mmol) were added to 15 ml of 1-propanol. The solution was warmed to 50°C and $W(CO)_4(pip)_2$ (0.500 g, 1.07 mmol) was added. The solution was warmed to reflux. The solution turned dark purple. After 30 min the solvent was removed by rotary evaporator. CH_2Cl_2 (20 ml) was added to the residue. The solution was washed three times each with 1 M HCl, saturated $NaHCO_3$ and then water. The organic layer was dried with magnesium sulfate and reduced in volume. Hexane was layered over the surface and the flask was placed in the refrigerator overnight. Filtration left a dark red or black crystalline solid. **1a**: 79% yield. IR (CH_2Cl_2): 2010(s), 1901(vs), 1884(sh), 1835(s), 1731 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6W$; C, 35.88; H, 2.81; N, 5.58. Found: C, 35.96; H, 2.82; N, 5.61. **2a**: 45% yield. IR (CH_2Cl_2): 2010(s), 1901(vs), 1880(sh), 1835(s), 1738 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6W$; C, 35.88; H, 2.81; N, 5.58. Found: C, 35.73; H, 2.85; N, 5.62. **3a**: 61% yield. IR (CH_2Cl_2): 2012(s), 1899(vs), 1884(sh), 1839(s), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_2O_6W$; C, 37.23; H, 3.12; N, 5.43. Found: C, 37.40; H, 3.26; N, 5.52. **4a**: 49% yield. IR (CH_2Cl_2):

Table 6
^{1}H-NMR [a] for reported compounds

	H3	H4	H5	H6	H–C=N	α-C–H	Other
1a	7.84 d (7.7)	7.92 m	7.41 m	9.21 d (5.5)	8.92 s	4.41 t (6.0)	4.10 q (7.0), C*H*$_2$CH$_3$, 3.20 t (6.0) CH$_2$C=O, 1.21 t (7.0) CH$_3$
1b	7.77 d (7.7)	7.91 m	7.43 m	9.10 d (5.2)	8.60	4.28 t (6.0)	4.10 q (7.2), C*H*$_2$CH$_3$, 3.18 t (6.1), CH$_2$C=O, 1.21 t (7.2), CH3
1c	7.71 d (7.8)	7.84 m	7.36 m	9.20 d (5.4)	8.54	4.37 t (6.2)	4.06 q (7.2), C*H*$_2$CH$_3$, 3.19 t (6.2), CH$_2$C=O, 1.22 t (7.2), CH$_3$
2a	7.89 m [b]	– [b]	7.42 m	9.27 d (5.8)	8.93 s	4.97 q (6.7)	4.31 m, CH$_2$, 1.85 d (6.9), CHC*H*$_3$, 1.35 t (7.1) CH$_2$C*H*$_3$
2b	7.82 d (7.8)	7.94 m	7.46 m	9.14 d (5.1)	8.61 s	4.79 q (6.9)	4.35 m, CH$_2$, 1.83 d (6.9) CHC*H*$_3$, 1.34 t (7.1), CHC*H*$_3$
3a	7.90 m [b]	– [b]	7.41 m	9.24 d (5.5)	9.02 s	4.54 d (10.5)	3.84 s, CH$_3$, 2.70 m, C*H*(CH$_3$)$_2$, 1.13 d (6.5), CH(C*H*$_3$)$_2$, 1.01 d (6.5), CH(C*H*$_3$)$_2$
3b	7.82 d (7.7)	7.90 m	7.45 m	9.15 d (5.2)	8.65 s	4.30 d (10.2)	3.84 s, CH$_3$, 2.73 m, C*H*(CH$_3$)$_2$, 1.13 d (6.5), C*H*(CH$_3$)$_2$, 0.97 d (6.5), CH(C*H*$_3$)$_2$
3c	7.82 m [b]	– [b]	7.37 m	9.21 d (4.2)	8.65 m	4.66 d (10.1)	3.85 s, CH$_3$, 2.67 m, C*H*(CH$_3$)$_2$, 1.11 d (6.3), CH(C*H*$_3$)$_2$, 1.04 d (6.4), CH(C*H*$_3$)$_2$
4a	7.93 m [b]	– [b]	7.46 m	9.25 d (5.5)	9.02 s	5.12, dd, (6.5, 4.4)	3.85 s, CH$_3$, 3.68 s, CH$_3$, 3.66 m, CH$_2$
4b	7.86, d (7.6)	7.95 m	7.48 m	9.12, d (5.3)	8.69 s	5.01 dd (9.4, 4.3)	3.86 s, CH$_3$, 3.66 s, CH$_3$, 3.57 m, CH$_2$
4c	7.80 d (7.4)	7.88 m	7.37 m	9.24 d (5.3)	8.62 s	5.15 dd (8.5, 5.2)	3.88 s, CH$_3$, 3.68 s, CH$_3$, 3.60 m, CH$_2$
5a	7.83 d (7.7)	7.94 m	7.41 m	9.24 d	8.78 s	4.24 t (6.5)	3.72 s, CH$_3$, 1.69, m, CH$_2$–C*H*$_2$–CH$_2$, 2.43 t, (6.8), CH$_2$CH$_2$C=O
6a	7.94 m [b]	– [b]	7.42 m	9.24 d (5.5)	–	4.43 t (7.0)	4.13 q (7.0), CH$_2$, 3.17 t (7.0), CH$_2$C=O, 2.62 s, py-CH$_3$, 1.25 t, (7.0), CH$_3$
7a	7.82 d (7.8)	7.94 m	7.39 m	9.23 d (5.4)	8.78 s	–	4.20 q (7.2), CH$_2$, 1.62 t (7.2), CH$_3$
8a	7.88 d (7.5)	7.66 m	7.24 m	8.57 d (5.6)	8.36 s	3.90 t (6 9)	4.07 q (7.1), C*H*$_2$CH$_2$, 3.88 t (6.9), CH$_2$C=O, 1.17 t (7.1), CH$_3$

[a] Recorded $CDCl_3$. See Fig. 1 for adopted numbering scheme.
[b] Signals from H^3 and H^4 overlap.

Table 7
Absorbance maxima for metal compounds in toluene and methanol and solvatochromism

Compound	Toluene [a]	Methanol [a]	Δ [b]
1a	538 (9400)	508 (8500)	1098
1b	524 (12 000)	491 (6900)	1283
1c	560 (11 000)	528 (5600)	1082
2a	556 (7900)	520 (5200)	1245
2b	547	505 (4400)	1520
3a	559 (8000)	526 (7300)	1122
3b	550 (6400)	510 (4600)	1426
3c	584 (6400)	547	1158
4a	558 (8600)	525 (7300)	1127
4b	544 (5900)	509 (5400)	1264
4c	581 (6500)	544 (5200)	1171
5a	541	511	1085
6a	525 (6700)	492 (6100)	1278
7a	542 (9500)	508 (7700)	1235

[a] λ_{max} in nm (ε in M^{-1} cm^{-1}).
[b] Difference in cm^{-1} between MLCT band in toluene and methanol.

2012(s), 1904(vs), 1887(sh), 1841(s), 1746 (sh, ester), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{14}N_2O_8W$; C, 35.19; H, 2.51; N, 4.98. Found: C, 35.35; H, 2.64; N, 5.08.

3.4. Synthesis of *1b–4b*

The amino acid H-xxx-OR·HCl (1.07 mmol), pyridine-2-carboxaldehyde (0.115 g, 1.07 mmol) and NEt_3 (0.108 g, 1.07 mmol) were added to 15 ml of 1-propanol. The solution was warmed gently then $Mo(CO)_4(pip)_2$ (1.07 mmol) was added. The solution rapidly turned dark purple. After 15 min the solvent was removed. The compound was purified following the procedure for the tungsten derivatives. **1b**: 76% yield. IR (CH_2Cl_2): 2018(s), 1913(vs), 1888(sh), 1839(s), 1731 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6Mo$; C, 43.49; H, 3.41; N, 6.76. Found: C, 43.47; H, 3.42; N, 6.72. **2b**: 80% yield. IR (CH_2Cl_2): 2017(s), 1913(vs), 1889(sh), 1842(s), 1738 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6Mo$; C, 43.49; H, 3.41; N, 6.76. Found: C, 43.05; H, 3.42; N, 6.72. **3b**: 69% yield. IR (CH_2Cl_2): 2015(s), 1911(vs), 1890(sh), 1842(s), 1753 (sh, ester), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_2O_6Mo$; C, 44.87; H, 3.77; N, 6.54. Found: C, 44.64; H, 3.72; N, 6.49. **4b**: 65% yield. IR (CH_2Cl_2): 2019(s), 1915(vs), 1890(sh), 1842(s), 1749 (sh, ester), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{14}N_2O_8Mo$; C, 41.94, H, 3.08; N, 6.11. Found: C, 41.81; H, 2.91; N, 6.10.

3.5. Synthesis of *1c*, *3c*, *4c*

In a typical procedure, the amino acid H-xxx-OR·HCl (0.667 mmol), pyridine-2-carboxaldehyde (0.071 g, 0.667 mmol) and NEt_3 (0.067 g, 0.667 mmol) were added to 15 ml of 1-propanol. The solution was warmed to 50°C and $[NEt_4][Cr(CO)_5I]$ (0.300 g, 0667 mmol) was added causing the solution to rapidly become dark purple. The solution was warmed to reflux. After 15 min the solvent was removed. The compound was purified following the procedure for the tungsten derivatives. **1c**: 38% yield. IR (CH_2Cl_2): 2010(s), 1910(vs), 1890(sh), 1838(s), 1733 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6Cr$; C, 48.66; H, 3.81; N, 7.57. Found: C, 48.68; H, 3.83; N, 7.59. **3c**: 41% yield. IR (CH_2Cl_2): 2010(s), 1908(vs), 1894(sh), 1840(s), 1753 (m, ester), 1736 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_2O_6Cr$; C, 50.01; H, 4.20; N, 7.29. Found: C, 49.51; H, 4.21; N, 7.17. **4c**: 46% yield. IR (CH_2Cl_2): 2013(s), 1911(vs), 1891(sh), 1840(s), 1748 (sh, ester) 1734 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{14}N_2O_8Cr$; C, 46.39; H, 3.41; N, 6.76. Found: C, 46.37; H, 3.43; N, 6.72.

3.6. Synthesis of *5a*

$SOCl_2$ (9.34 g, 78.6 mmol) was added to 50 ml of methanol cooled to 0°C. After the solution was warmed to room temperature (r.t.) 4-aminobutyric acid (GABA; 6.54 g, 63.4 mmol) was added. The clear solution was stirred and then refluxed for 1 h. The solution was removed producing H_2N–$(CH_2)_3$–OMe·HCl as a white fluffy solid. **5a** was then prepared and purified using the procedure described for **1a**–**4a**. An oil resulted which resisted attempts to obtain a crystalline solid.**5a**: IR (CH_2Cl_2): 2007(s), 1899(vs), 1882(sh), 1837(s), 1739 (m, ester) cm^{-1}. Anal. Calc. for $C_{15}H_{14}N_2O_6W$; C, 35.88; H, 2.82; N, 5.58. Found: C, 35.95; H, 2.61; N, 5.59.

3.7. Synthesis of *6a*

$W(CO)_4(pip)_2$ (0.500 g, 1.07 mmol) was mixed with stoichiometric amounts of H-β-ala-OEt·HCl, NEt_3, and 2-acetylpyridine in 1-propanol. The solution was refluxed for 75 min. The product was purified and isolated as described for **1a**–**4a**. A red–brown solid was obtained. **6a**: 33% yield. IR (CH_2Cl_2): 2008(s), 1895(vs), 1878(sh), 1834(s), 1734 (m, ester) cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_2O_6W$; C, 37.23; H, 3.12; N, 5.43. Found: C, 37.11; H, 3.19; N, 5.40.

3.8. Synthesis of *7a*

H_2NEt was bubbled from a lecture bottle into a 25 ml solution of 1-propanol containing 0.115 g (1.07 mmol) pyridine-2-carboxaldehyde for 5 min. The solution was warmed to 50°C to promote diimine formation. $W(CO)_4(pip)_2$ (0.500 g, 1.07 mmol) was added to the solution. The solution was heated to reflux and turned a dark purple color. After 30 min of reflux the solvent was removed. The product was isolated follow-

ing the procedure for other tungsten derivatives. **7a**: 26% yield. IR (CH_2Cl_2): 2007(s), 1899(vs), 1886(sh), 1835(s) cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_2O_6W$; C, 33.51; H, 2.34; N, 6.51. Found: C, 33.67; H, 2.43; N, 6.56.

3.9. Synthesis of **8**

The free ligand containing the β-alanine ethyl ester conjugate was prepared to obtain NMR information by mixing of H-β-ala-OEt·HCl (0.166 g, 1.32 mmol) and NEt_3 (0.110 g, 1.09 mmol) in CH_2Cl_2. The solution was filtered. The solvent was removed. Benzene, pyridine-2-carboxaldehyde (0.113 g, 1.05 mmol) and molecular sieves to absorb water produced during the condensation reaction were added. The solution was stirred overnight. The solvent was removed and the colorless oil was dried overnight on a vacuum pump.

3.10. X-ray structure determination of **1b**

Black crystals of **1b** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution containing the compound. A single crystal having dimensions of $0.8 \times 0.6 \times 0.5$ mm was selected for analysis by a Siemens SMART diffractometer. Data were collected using Mo-K_α radiation at 120(1) K. The structures were solved using direct methods [45]. Metal and coordinated atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber [46], and anomalous dispersion corrections were taken from Creagh and McAuley [47]. All calculations were performed using SHELXTL or SHELX-93 [48].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 112872. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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